Supporting Information for

Enantio-, Diastereo- and Regioselective Iridium-Catalyzed Asymmetric Allylic Alkylation of Acyclic β-Ketoesters.

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Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and 600 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm) or C_6HD_5 (δ 7.16 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm) or C_6HD_5 (δ 128.06 ppm). ^{31}P and ^{19}F NMR spectra were recorded on a Varian Mercury 300 MHz (at 121 MHz and 282 MHz, respectively). ^{19}F NMR spectra were reported relative to $CFCl_3$ (δ 0.0 ppm). ^{31}P NMR spectra were reported relative to external H_3PO_4 (δ 0.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent). Analytical HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak (AD-H or AS) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from

[1] A. M. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, **1996**, *15*, 1518.

Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Ligands **L3**–**L6**,[2] allyl carbonates,[3] and β-ketoesters[4] were prepared by known methods.

List of Abbreviations:

ee – enantiomeric excess, dr – diastereomeric ratio, HPLC – high-performance liquid chromatography, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, THF – tetrahydrofuran, IPA – isopropanol, TBD – 1,5,7-triazabicyclo[4.4.0]dec-5-ene, DABCO – 1,4-diazabicyclo[2.2.2]octane, cod – *cis,cis*-1,5-cyclooctadiene, DMAP – 4-(dimethylamino)pyridine

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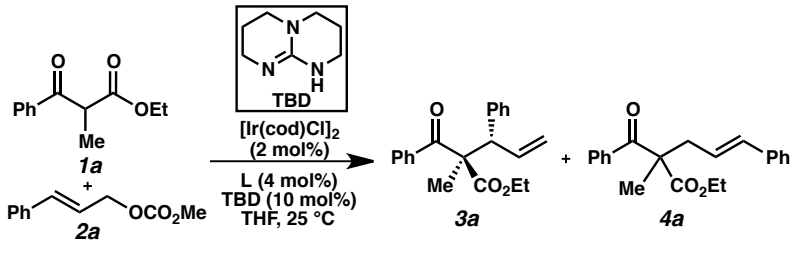
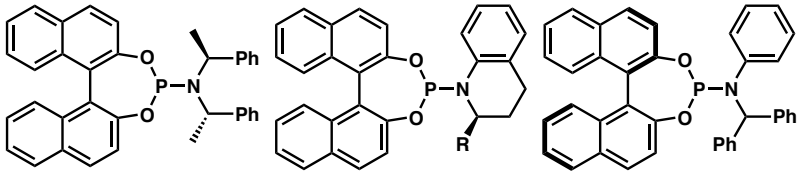
[2] (a) Liu, W.-B.; He, H.; Dai, L.-X.; You, S.-L. *Synthesis*, **2009**, 2076. (b) Liu, W.-B.; Zheng, C.; Zhuo, C.-X.; Dai, L.-X.; You, S.-L. *J. Am. Chem. Soc.* **2012**, *134*, 4812.

[3] (a) Wuts, P. G. M.; Ashford, S. W.; Anderson, A. M.; Atkins, J. R. *Org. Lett.* **2003**, *5*, 1483. (b) Malkov, A. V.; Gouriou, L.; Lloyd-Jones, G. C.; Starý, I.; Langer, V.; Spoor, P.; Vinader, V.; Kočovský, P. *Chem. Eur. J.* **2006**, *12*, 6910.

[4] (a) González, D. F.; Brand, J. P.; Waser, J. *Chem. Eur. J.* **2010**, *16*, 9457. (b) Bartoli, G.; Bosco, M.; Bellucci, M. C.; Marcantoni, E.; Sambri, L.; Torregiani, E. *Eur. J. Org. Chem.* **1999**, 617. (c) Stavber, G.; Zupan, M.; Stavber, S. *Tetrahedron Lett.* **2007**, *48*, 2671. (d) Meshram, H. M.; Reddy, P. N.; Sadashiv, K.; Yadav, J. S. *Tetrahedron Lett.* **2005**, *46*, 623. (e) Turner, J. A.; Jacks, W. S. *J. Org. Chem*, **1989**, *54*, 4229.

Optimization of Reaction Parameters (Table S1)





(S,S,Sa)-L1
(S,S,Ra)-L2

R = Me: (R, Ra)-L3
R = Me: (R, Sa)-L4
R = H: (Ra)-L5

(Ra)-L6

entry	*L*	base/additive (x equiv)	time (h)	conv. (%)[b]	yield (%)[c]	*3a:4a*[b]	dr of *3a*[b]	ee of *3* (%)[d]
1	*L1*	NaH (2)	22	91	–	89:11	1:1.8	81(97)
2	*L2*	NaH (2)	48	46	–	17:83	1:1	-
3	*L3*	NaH (2)	22	>95	64	95:5	13:1	99
4	*L4*	NaH (2)	48	34	–	42:58	3.5:1	-
5	*L5*	NaH (2)	72	>95	–	71:29	2:1	76
6	*L6*	NaH (2)	72	>95	–	93:7	7.3:1	72
7	*L3*	LiBr (1)	32	>95	91	95:5	>20:1	>99
8	*L3*	LiO*t*-Bu (2)	2	>95	97	93:7	>20:1	98
9	*L3*	KO*t*-Bu (2)	4	>95	–	93:7	2:1	94(87)
10	*L3*	Cs_2CO_3 (2)	4	>95	–	83:17	1:2.2	87(94)
11	*L3*	DABCO (2)	24	>95	–	81:19	1:2.7	64(82)
12	*L3*	proton sponge (2)	4	>95	–	90:10	1:1	87(93)
13	*L3*	DMAP (2)	4	>95	–	83:17	1:1.4	91(93)
14	*L3*	Bu_4NBr (1)	3	>95	–	88:12	1:2.6	87(93)
15	*L3*	$BnMe_3NBr$ (1)	4	>95	–	86:14	1:1	91(95)

[a] Reactions performed with 0.1 mmol of **2a**, 0.2 mmol of **1a** in 1 mL of THF. [b] Determined by ^{1}H NMR or UHPLC-MS analysis of the crude reaction mixture. [c] Isolated yield. [d] (ee) of the alternative diastereomer.

General Procedure for Optimization Reaction (Table S1): All experiments were performed in a nitrogen-filled glove box.

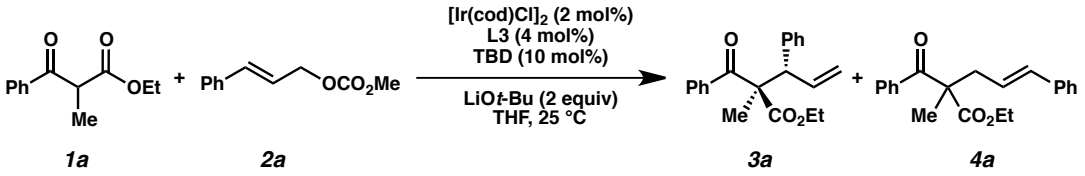
Procedure A (for entries 1-9): $[Ir(cod)Cl]_2$ (1.4 mg, 0.002 mmol, 2 mol%), ligand **L** (0.004 mmol, 4 mol%), and TBD (1.4 mg, 0.01 mmol, 10 mol%) were added to a 2 dram scintillation vial (vial A) equipped with a magnetic stirring bar. The vial was then charged with THF (0.5 mL) and stirred at 25 °C for 10 min, generating an orange solution. To another 2 dram scintillation vial (vial B) was added base (0.2 mmol, 2 equiv), 0.5 mL of THF and β-ketoester **1a** (41.2 mg, 0.2 mmol, 2.0 equiv). After stirring

for 10 min at 25 °C, the pre-formed catalyst solution (vial A) was transferred to vial B, and cinnamyl carbonate (**2a**) (19.2 mg, 0.1 mmol, 1.0 equiv) was added. The vial was sealed and stirred at 25 °C until allylic carbonate **2a** was fully consumed, as indicated by UHPLC-MS analysis. Upon completion of the reaction the vial was removed from the glovebox and uncapped. Saturated NH_4Cl aqueous solution was added and the mixture was extracted with CH_2Cl_2 (10 mL x 3), the combined organic phase was washed with brine, dried over Mg_2SO_4, filtered and concentrated *in vacuo*. The regioselectivity (branched product to linear product, b:l) and diastereoselectivity (dr) were determined by ^{1}H NMR. The residue was purified by silica gel flash chromatography (gradient elution, 0→1→2% EtOAc in hexanes) to afford the desired product.

Procedure B (for entries 10-15): $[Ir(cod)Cl]_2$ (1.4 mg, 0.002 mmol, 2 mol%), ligand **L** (0.004 mmol, 4 mol%), and TBD (1.4 mg, 0.01 mmol, 10 mol%) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. The vial was then charged with THF (0.5 mL) and stirred at 25 °C for 10 min, generating an orange solution. Cinnamyl carbonate (**2a**) (19.2 mg, 0.1 mmol, 1.0 equiv), β-ketoester **1a** (41.2 mg, 0.2 mmol, 2.0 equiv), base (0.2 mmol, 2 equiv) or additive (0.1 mmol, 1.0 equiv) and an additional 0.5 mL of THF were added. The vial was sealed and stirred at 25 °C until allylic carbonate **2a** was fully consumed, as indicated by UHPLC-MS analysis. Upon completion of the reaction the vial was removed from the glovebox and uncapped and THF evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a celite pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) and diastereoselectivity (dr) were determined by ^{1}H NMR. The residue was purified by silica gel flash chromatography (gradient elution, 0→1→2% EtOAc in hexanes) to afford the desired product.

General Procedure for the Ir-Catalyzed Asymmetric Allylic Alkylation of Acyclic β-Ketoesters

Please note that the absolute configuration was determined only for compound **3f** *via X-ray analysis of its derivative (vide infra). The absolute configuration for all other products* ***3*** *has been inferred by analogy. Isolated yields are reported in Tables 2 and 3 (see manuscript). For respective SFC conditions, please refer to Table S2.*



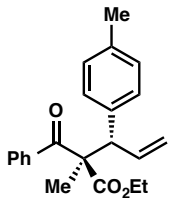
In a nitrogen-filled glove box, $[Ir(cod)Cl]_2$ (1.4 mg, 0.002 mmol, 2 mol%), ligand **L3** (1.8 mg, 0.004 mmol, 4 mol%), and TBD (1.4 mg, 0.01 mmol, 10 mol%) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. The vial was then charged with THF (0.5 mL) and stirred at 25 °C for 10 min, generating an orange solution. To another 2 dram scintillation vial was added LiO*t*-Bu (16.0 mg, 0.2 mmol, 2 equiv) and 0.5 mL of THF, then β-ketoester **1a** (41.2 mg, 0.2 mmol, 2.0 equiv) was added. After stirring for 10 min, the above pre-formed catalyst solution was transferred to this vial, followed by cinnamyl carbonate (**2a**) (19.2 mg, 0.1 mmol, 1.0 equiv). The vial was sealed and stirred at 25 °C until allylic carbonate **2a** was fully consumed, as indicated by UHPLC-MS analysis. Upon completion of the reaction the vial was removed from the glovebox and uncapped and saturated NH_4Cl aqueous solution was added. The mixture was extracted with CH_2Cl_2 (10 mL x 3), the combined organic layers washed with brine, dried over Mg_2SO_4, filtered and concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l = 93:7) and diastereoselectivity (dr >20:1) were determined by ^1H NMR of the crude reaction mixture. The residue was purified by silica gel flash chromatography (gradient elution, 0→1→2% EtOAc in hexanes) to afford product (31.2 mg, 97% yield) as a colorless oil.

Ethyl-(2*R*,3*S*)-2-benzoyl-2-methyl-3-phenylpent-4-enoate (3a).

Ketoester **3a** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +76.6 (*c* 0.77, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.60 (m, 2H), 7.52–7.43 (m, 1H), 7.38–7.33 (m, 2H), 7.26–7.15 (m, 5H), 6.35 (ddd, *J* = 17.0, 10.3, 8.3 Hz, 1H), 5.13 (ddd, *J* = 10.2, 1.7, 0.9 Hz, 1H), 5.07 (ddd, *J* = 17.0, 1.8, 1.2 Hz, 1H), 4.39 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.09 (qd, *J* = 7.2, 0.6 Hz, 2H), 1.53 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 173.0, 139.5, 137.8, 137.2, 132.3, 130.1, 128.4, 128.20, 128.17, 127.1, 117.5, 61.8, 61.6, 54.8, 21.0, 13.8; IR (Neat Film, NaCl) 3062, 3028, 2981, 2939, 2902, 1731, 1686, 1682, 1597, 1582, 1493, 1452, 1446, 1377, 1311, 1243, 1218, 1186, 1096, 1018, 1001, 962, 920, 860, 758 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1642, found 323.1647; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 4.12, minor = 6.14.

Spectroscopic Data for Ir-Catalyzed Allylic Alkylation Products

Ethyl (2*R*,3*S*)-2-benzoyl-2-methyl-3-(*p*-tolyl)pent-4-enoate (3b).

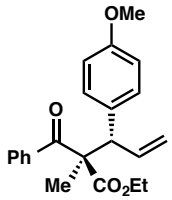


3b

Ketoester **3b** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ +80.4 (*c* 1.82, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.65 (m, 2H), 7.47 (ddt, *J* = 8.6, 7.0, 1.3 Hz, 1H), 7.39–7.33 (m, 2H), 7.11–7.02 (m, 4H), 6.33 (ddd, *J* = 16.9, 10.2, 8.3 Hz, 1H), 5.11 (ddd, *J* = 10.3, 1.8, 1.0 Hz, 1H), 5.07 (ddd, *J* = 17.0, 1.9, 1.2 Hz, 1H), 4.38 (dd, *J* = 8.3, 1.2 Hz, 1H), 4.09 (qd, *J* = 7.1, 2.6 Hz, 2H), 2.29 (s, 3H), 1.54 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 173.0, 137.9, 137.2, 136.6, 136.4, 132.3, 129.9, 128.9, 128.4, 128.2, 117.3, 61.8, 61.5, 54.3, 21.1, 20.9, 13.8; IR (Neat Film, NaCl) 3058, 3023, 2981, 2938, 1736, 1732, 1682, 1687, 1636, 1597, 1580, 1513, 1446,

1376, 1310, 1243, 1219, 1186, 1115, 1104, 1021, 1001, 963, 919, 820, 793 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798, found 337.1805; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 6.71, minor = 9.45.

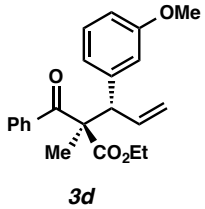
Ethyl (2*R*,3*S*)-2-benzoyl-3-(4-methoxyphenyl)-2-methylpent-4-enoate (3c).



3c

Ketoester **3c** was isolated by silica gel chromatography (gradient elution, 2→5% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +81.5 (*c* 2.02, $CHCl_3$); R_f = 0.2 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.63 (m, 2H), 7.52–7.43 (m, 1H), 7.38–7.32 (m, 2H), 7.15–7.08 (m, 2H), 6.85–6.74 (m, 2H), 6.32 (ddd, *J* = 17.0, 10.3, 8.2 Hz, 1H), 5.11 (ddd, *J* = 10.3, 1.8, 1.0 Hz, 1H), 5.05 (ddd, *J* = 17.0, 1.8, 1.2 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 4.09 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.76 (s, 3H), 1.51 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 173.0, 158.5, 138.0, 137.3, 132.3, 131.4, 131.1, 128.4, 128.2, 117.2, 113.5, 61.9, 61.5, 55.3, 53.9, 20.8, 13.9; IR (Neat Film, NaCl) 3067, 2981, 2937, 2904, 2835, 1731, 1686, 1682, 1610, 1597, 1581, 1511, 1446, 1376, 1302, 1245, 1218, 1181, 1114, 1101, 1034, 963, 922, 830 cm^{-1}; HRMS (ESI+) *m/z* calc'd for fragment $C_{10}H_{11}O$ $[M-C_{11}H_{12}O_3+H]^+$: 147.0804, found 147.0808; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 11.17, major = 12.67.

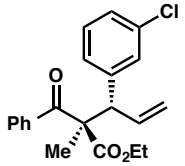
Ethyl (2*R*,3*S*)-2-benzoyl-3-(-methoxyphenyl)-2-methylpent-4-enoate (3d).



3d

Ketoester **3d** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +85.1 (*c* 1.21, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.63 (m, 2H), 7.52–7.43 (m, 1H), 7.42–7.32 (m, 2H), 7.23–7.11 (m, 1H), 6.82–6.71 (m, 3H), 6.32 (ddd, *J* = 16.9, 10.3, 8.3 Hz, 1H), 5.13 (ddd, *J* = 10.3, 1.8, 0.9 Hz, 1H), 5.09 (ddd, *J* = 17.0, 1.8, 1.2 Hz, 1H), 4.37 (dt, *J* = 8.3, 1.1 Hz, 1H), 4.09 (qd, *J* = 7.2, 1.3 Hz, 2H), 3.74 (s, 3H), 1.53 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 172.9, 159.3, 141.0, 137.6, 137.3, 132.3, 129.1, 128.4, 128.2, 122.4, 117.6, 116.0, 112.4, 61.8, 61.6, 55.2, 54.8, 21.0, 13.8; IR (Neat Film, NaCl) 3078, 2982, 2940, 2835, 1731, 1683, 1598, 1583, 1488, 1454, 1377, 1315, 1245, 1217, 1186, 1162, 1096, 1049, 1019, 1001, 963, 922, 861, 781 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1747, found 353.1761; SFC conditions: 2% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 12.24, minor = 13.50.

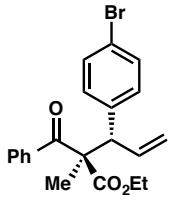
Ethyl (2*R*,3*S*)-2-benzoyl-3-(3-chlorophenyl)-2-methylpent-4-enoate (3e).



3e

Ketoester **3e** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ +99.1 (*c* 1.13, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.63 (m, 2H), 7.48 (ddt, *J* = 7.8, 6.9, 1.2 Hz, 1H), 7.41–7.33 (m, 2H), 7.22–7.19 (m, 1H), 7.19–7.14 (m, 2H), 7.14–7.08 (m, 1H), 6.30 (ddd, *J* = 17.0, 10.2, 8.4 Hz, 1H), 5.15 (ddd, *J* = 10.3, 1.6, 0.9 Hz, 1H), 5.07 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.34 (d, *J* = 8.4 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.52 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 172.6, 141.7, 137.0, 136.9, 133.9, 132.5, 130.3, 129.3, 128.5, 128.4, 128.3, 127.2, 118.1, 61.7, 61.7, 54.5, 20.9, 13.8; IR (Neat Film, NaCl) 3068, 2982, 2943, 1732, 1682, 1595, 1574, 1475, 1446, 1378, 1301, 1245, 1218, 1194, 1095, 1018, 1001, 963, 924, 784 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}ClO_3$ $[M+H]^+$: 357.1252, found 357.1260; SFC conditions: 10% IPA, 4.0 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 1.59, minor = 1.77.

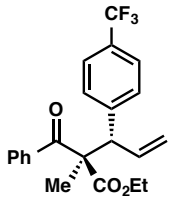
Ethyl (2*R*,3*S*)-2-benzoyl-3-(4-bromophenyl)-2-methylpent-4-enoate (3f).



3f

Ketoester **3f** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +89.0 (*c* 1.42, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70–7.63 (m, 2H), 7.50–7.45 (m, 1H), 7.40–7.33 (m, 4H), 7.13–7.08 (m, 2H), 6.29 (ddd, *J* = 16.9, 10.2, 8.2 Hz, 1H), 5.16–5.11 (m, 1H), 5.05 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.51 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 172.7, 138.6, 137.2, 136.9, 132.5, 131.9, 131.2, 128.5, 128.3, 121.1, 117.9, 61.7, 61.6, 54.1, 20.8, 13.8; IR (Neat Film, NaCl) 3077, 2981, 2938, 1728, 1683, 1597, 1488, 1446, 1377, 1305, 1243, 1217, 1186, 1099, 1076, 1010, 963, 922, 822, 802, 716 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}BrO_3$ $[M+H]^+$: 401.0747, found 401.0754; SFC conditions: 10% IPA, 4.0 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 2.95, major = 3.47.

Ethyl (2*R*,3*S*)-2-benzoyl-2-methyl-3-(4-(trifluoromethyl)phenyl)pent-4-enoate (3g).

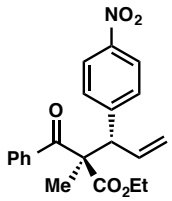


3g

Ketoester **3g** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +77.4 (*c* 0.94, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.63 (m, 2H), 7.53–7.45 (m, 3H), 7.39–7.35 (m, 4H), 6.33 (ddd, *J* = 16.9, 10.2, 8.4 Hz, 1H), 5.16 (ddd, *J* = 10.2, 1.6, 0.9 Hz, 1H), 5.07 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.44 (d, *J* = 8.4 Hz, 1H), 4.09 (q, *J* = 7.1 Hz,

2H), 1.53 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 172.6, 143.9, 136.9, 136.8, 132.6, 130.6, 129.2 (q, J = 32.4 Hz), 128.5, 128.3, 125.0 (q, J = 3.7 Hz), 124.3 (d, J = 271.8 Hz), 118.3, 61.8, 61.6, 54.6, 20.8, 13.8; IR (Neat Film, NaCl) 3070, 2984, 2941, 1732, 1687, 1682, 1617, 1597, 1581, 1446, 1413, 1379, 1327, 1245, 1220, 1166, 1123, 1069, 1018, 964, 924, 846 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{22}H_{22}F_3O_3$ $[M+H]^+$: 391.1516, found 391.1517; SFC conditions: 2% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 5.20, major = 6.68.

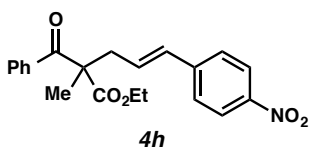
Ethyl (2*R*,3*S*)-2-benzoyl-2-methyl-3-(4-nitrophenyl)pent-4-enoate (3h).



3h

Ketoester **3h** was isolated by silica gel chromatography (5% EtOAc in hexanes) as a colorless oil. 93% ee, $[\alpha]_D^{25}$ +96.8 (*c* 0.64, $CHCl_3$); R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13–8.09 (m, 2H), 7.70–7.63 (m, 2H), 7.52–7.48 (m, 1H), 7.46–7.43 (m, 2H), 7.40–7.35 (m, 2H), 6.31 (ddd, J = 16.9, 10.2, 8.5 Hz, 1H), 5.23–5.16 (m, 1H), 5.08 (dt, J = 17.0, 1.3 Hz, 1H), 4.50 (d, J = 8.5 Hz, 1H), 4.10 (qd, J = 7.1, 2.4 Hz, 2H), 1.54 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 172.3, 147.4, 146.8, 136.3, 136.1, 132.6, 131.0, 128.4, 128.2, 123.1, 118.8, 61.8, 61.4, 54.3, 20.5, 13.7; IR (Neat Film, NaCl) 3080, 2982, 2942, 1731, 1686, 1682, 1597, 1523, 1519, 1446, 1379, 1346, 1245, 1219, 1111, 1001, 1015, 964, 926, 853 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}O_5N$ $[M+H]^+$: 368.1492, found 368.1508; SFC conditions: 5% MeOH, 3.0 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 4.47, major = 5.71.

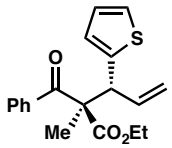
Ethyl (*E*)-2-benzoyl-2-methyl-5-(4-nitrophenyl)pent-4-enoate (4h).



4h

Ketoester **4h** was isolated by silica gel chromatography (5% EtOAc in hexanes) as a yellow solid. 23% ee, $[\alpha]_D^{25}$ +4.7 (*c* 0.96, $CHCl_3$); R_f = 0.3 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (dt, *J* = 9.0, 2.5 Hz, 2H), 7.86 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.59–7.49 (m, 1H), 7.47–7.40 (m, 4H), 6.45 (dt, *J* = 15.9, 1.2 Hz, 1H), 6.32 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.12 (qd, *J* = 7.2, 1.1 Hz, 2H), 3.00 (ddd, *J* = 14.2, 7.3, 1.3 Hz, 1H), 2.90 (ddd, *J* = 14.2, 7.7, 1.2 Hz, 1H), 1.58 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 173.6, 146.9, 143.6, 135.4, 133.1, 132.1, 130.0, 128.7, 126.8, 124.1, 61.7, 57.3, 40.6, 21.6, 14.0; IR (Neat Film, NaCl) 2981, 2936, 1732, 1686, 1682, 1596, 1519, 1515, 1446, 1342, 1298, 1267, 1239, 1184, 1108, 973, 857 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}O_5N$ $[M+H]^+$: 368.1492, found 368.1499; SFC conditions: 10% MeOH, 3.0 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 7.13, minor = 8.06.

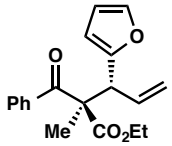
Ethyl (2*R*,3*R*)-2-benzoyl-2-methyl-3-(thiophen-2-yl)pent-4-enoate (3i).



3i

Ketoester **3i** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. 95% ee, $[\alpha]_D^{25}$ +53.0 (*c* 1.63, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.74–7.68 (m, 2H), 7.51–7.47 (m, 1H), 7.42–7.35 (m, 2H), 7.16 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.84 (ddd, *J* = 3.5, 1.2, 0.7 Hz, 1H), 6.23 (ddd, *J* = 16.4, 10.6, 9.0 Hz, 1H), 5.23–5.16 (m, 2H), 4.77 (d, *J* = 9.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.52 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.5, 172.3, 142.1, 136.8, 136.6, 132.5, 128.5, 128.4, 126.9, 126.2, 124.9, 118.2, 62.2, 61.9, 49.8, 19.4, 13.9; IR (Neat Film, NaCl) 3069, 2981, 2937, 1732, 1687, 1682, 1597, 1580, 1446, 1383, 1298, 1246, 1221, 1107, 1018, 1001, 968, 924, 851, 795, 747 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{19}H_{21}O_3S$ $[M+H]^+$: 329.1206, found 329.1214; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 7.92, minor = 11.24.

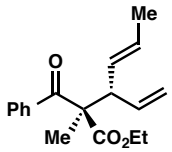
Ethyl (2*R*,3*R*)-2-benzoyl-3-(furan-2-yl)-2-methylpent-4-enoate (3j).



3j

Ketoester **3j** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +67.3 (*c* 1.34, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73–7.67 (m, 2H), 7.52–7.45 (m, 1H), 7.40–7.35 (m, 2H), 7.27 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.25 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.17 (ddd, *J* = 17.0, 10.2, 8.5 Hz, 1H), 6.11 (dt, *J* = 3.3, 0.7 Hz, 1H), 5.19 (ddd, *J* = 10.2, 1.7, 0.8 Hz, 1H), 5.14 (ddd, *J* = 17.0, 1.7, 1.1 Hz, 1H), 4.62 (dd, *J* = 8.5, 0.9 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 1.52 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 172.1, 152.9, 141.5, 136.6, 134.4, 132.2, 128.3, 128.2, 118.3, 110.1, 108.7, 61.6, 61.4, 47.9, 19.3, 13.8; IR (Neat Film, NaCl) 3081, 2983, 2941, 2904, 1732, 1686, 1597, 1581, 1501, 1446, 1378, 1301, 1246, 1222, 1149, 1096, 1013, 968, 926, 885, 860, 797, 736 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{21}O_4$ $[M+H]^+$: 313.1431, found 313.1438; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 5.09, minor = 9.14.

Ethyl (2*R*,3*S*,*E*)-2-benzoyl-2-methyl-3-vinylhex-4-enoate (3k).

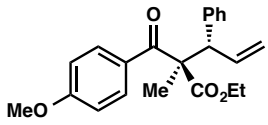


3k

Ketoester **3k** was isolated by silica gel chromatography (gradient elution, 0→1→2% EtOAc in hexanes) as a colorless oil. 91% ee, $[\alpha]_D^{25}$ +43.5 (*c* 1.86, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.71 (m, 2H), 7.52–7.46 (m, 1H), 7.42–7.36 (m, 2H), 5.98 (ddd, *J* = 16.9, 10.5, 7.5 Hz, 1H), 5.47–5.27 (m, 2H), 5.15–5.00 (m, 2H), 4.09 (qd, *J* = 7.1, 1.5 Hz, 2H), 3.73–3.69 (m, 1H), 1.65–1.58 (m, 3H), 1.48 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 173.0, 137.2, 136.8, 132.4, 129.0, 128.5, 128.4, 128.3, 117.1, 61.4, 60.5, 51.6, 19.2, 18.2, 14.0; IR (Neat Film, NaCl) 3077, 2981, 2939, 2913, 1732, 1687, 1682, 1597, 1580, 1446, 1377, 1299, 1245,

1221, 1100, 1018, 1001, 970, 921, 859 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found 287.1654; SFC conditions: 2% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.40, major = 5.52.

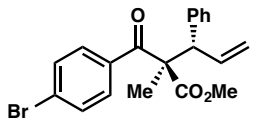
Ethyl (2*R*,3*S*)-2-(4-methoxybenzoyl)-2-methyl-3-phenylpent-4-enoate (3l).



3l

Ketoester **3l** was isolated by silica gel chromatography (4% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ +53.9 (*c* 1.51, $CHCl_3$); R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.76–7.69 (m, 2H), 7.25–7.17 (m, 5H), 6.87–6.82 (m, 2H), 6.36 (ddd, *J* = 17.0, 10.3, 8.1 Hz, 1H), 5.12 (ddd, *J* = 10.3, 1.8, 1.0 Hz, 1H), 5.05 (ddd, *J* = 17.0, 1.8, 1.2 Hz, 1H), 4.39 (dt, *J* = 8.1, 1.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.53 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 173.4, 162.9, 139.6, 138.0, 130.8, 130.2, 129.5, 128.1, 127.0, 117.3, 113.6, 61.5, 61.3, 55.5, 54.7, 21.0, 13.9; IR (Neat Film, NaCl) 3083, 2981, 2940, 2842, 1727, 1677, 1600, 1576, 1513, 1454, 1417, 1376, 1310, 1247, 1221, 1176, 1118, 1031, 964, 842 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1747, found 353.1752; SFC conditions: 10% IPA, 4.0 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 2.67, minor = 3.51.

Methyl (2*R*,3*S*)-2-(4-bromobenzoyl)-2-methyl-3-phenylpent-4-enoate (3m).

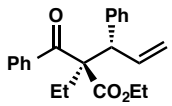


3m

Ketoester **3m** was isolated by silica gel chromatography (gradient elution, 1→2 Et_2O in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +65.9 (*c* 0.50, $CHCl_3$); R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.48 (m, 4H), 7.29–7.09 (m, 5H), 6.31 (ddd, *J* = 16.9, 10.3, 8.4 Hz, 1H), 5.21–4.96 (m, 2H), 4.37 (d, *J* = 8.5 Hz, 1H), 3.62 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 173.3, 139.1, 137.3, 135.7, 131.7, 130.0, 129.7, 128.2, 127.5, 127.1, 117.7, 61.8, 54.7, 52.5, 20.8; IR (Neat Film,

NaCl) 3355, 3028, 2997, 2948, 1735, 1685, 1584, 1484, 1452, 1395, 1245, 1221, 1117, 1073, 966, 922, 841, 756 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{20}H_{20}BrO_3$ $[M+H]^+$: 387.0590, found 387.0612; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 5.35, minor = 5.88.

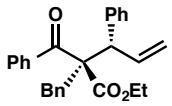
Ethyl (2*R*,3*S*)-2-benzoyl-2-ethyl-3-phenylpent-4-enoate (3n).



3n

Ketoester **3n** was isolated by silica gel chromatography (gradient elution, 0→2 Et_2O in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +77.4 (*c* 0.25, $CHCl_3$); R_f = 0.4 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.61–7.51 (m, 2H), 7.48–7.38 (m, 1H), 7.35–7.11 (m, 7H), 6.33 (ddd, *J* = 17.0, 10.3, 7.8 Hz, 1H), 5.07 (ddd, *J* = 10.3, 1.8, 1.1 Hz, 1H), 4.96 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.38 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.06 (qd, *J* = 7.2, 3.3 Hz, 2H), 2.15 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.89 (dq, *J* = 14.9, 7.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 172.9, 139.5, 138.4, 137.9, 132.0, 129.8, 128.2, 128.1, 127.9, 127.0, 116.6, 65.2, 61.0, 52.2, 27.6, 13.6, 8.5; IR (Neat Film, NaCl) 3061, 3028, 2980, 1729, 1679, 1597, 1446, 1386, 1303, 1228, 1208, 1097, 1028, 993, 917, 759 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798, found 337.1813; SFC conditions: 5% MeOH, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 2.48, minor = 2.20.

Ethyl (2*R*,3*S*)-2-benzoyl-2-benzyl-3-phenylpent-4-enoate (3o).

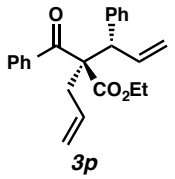


3o

Ketoester **3o** was isolated by silica gel chromatography (gradient elution, 1→2 EtOAc in hexanes) as a white solid. >99% ee, $[\alpha]_D^{25}$ +37.1 (*c* 1.29, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 1H), 7.29–7.21 (m, 4H), 7.17–7.10 (m, 8H), 7.04–7.00 (m, 2H), 6.37 (ddd, *J* = 17.0, 10.3, 8.1 Hz, 1H), 5.13 (ddd, *J* = 10.2, 1.8, 1.0 Hz, 1H), 5.02 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.42 (d, *J* = 7.9 Hz, 1H), 3.99 (dq,

J = 10.7, 7.1 Hz, 1H), 3.80 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.28 (AB, *J* = 15.5, 13.5 Hz, 2H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 172.0, 139.7, 139.3, 138.3, 136.8, 131.4, 131.2, 130.0, 128.4, 128.1, 127.7, 127.6, 127.4, 126.9, 117.6, 67.5, 61.0, 56.8, 42.1, 13.4; IR (Neat Film, NaCl) 3063, 3029, 2982, 2929, 1729, 1673, 1600, 1582, 1496, 1448, 1367, 1299, 1241, 1209, 1082, 1066, 1025, 925, 757 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{27}H_{27}O_3$ $[M+H]^+$: 399.1955, found 399.1956; SFC conditions: 4% IPA, 4.0 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 5.06, minor = 8.94.

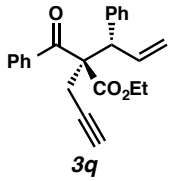
Ethyl (2*R*,3*S*)-2-allyl-2-benzoyl-3-phenylpent-4-enoate (3p).



3p

Ketoester **3p** was isolated by silica gel chromatography (2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +80.7 (*c* 0.31, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.49 (m, 2H), 7.43 (ddt, *J* = 7.7, 7.0, 1.2 Hz, 1H), 7.33–7.27 (m, 2H), 7.25–7.19 (m, 3H), 7.18–7.13 (m, 2H), 6.36 (ddd, *J* = 17.0, 10.3, 8.0 Hz, 1H), 5.71 (dddd, *J* = 17.0, 10.2, 7.8, 7.0 Hz, 1H), 5.10 (ddd, *J* = 10.3, 1.8, 1.1 Hz, 1H), 5.03 (ddt, *J* = 10.2, 2.1, 1.0 Hz, 1H), 4.99 (ddd, *J* = 17.0, 1.8, 1.2 Hz, 1H), 4.92 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.35 (dt, *J* = 8.0, 1.2 Hz, 1H), 4.14–3.96 (m, 2H), 2.86 (ddt, *J* = 14.6, 7.0, 1.3 Hz, 1H), 2.63 (ddt, *J* = 14.6, 7.7, 1.2 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 172.4, 139.4, 138.3, 138.2, 132.5, 132.1, 130.1, 128.3, 128.14, 128.12, 127.2, 119.5, 117.2, 65.2, 61.2, 53.4, 39.4, 13.7; IR (Neat Film, NaCl) 3079, 3029, 2981, 2933, 1728, 1679, 1638, 1597, 1581, 1493, 1446, 1367, 1257, 1216, 1181, 1144, 1045, 1023, 1001, 921, 758 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{25}O_3$ $[M+H]^+$: 349.1808, found 349.1808; SFC conditions: 3% IPA, 4.0 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 7.16, minor = 8.60.

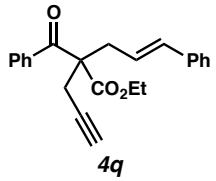
Ethyl (2*R*,3*S*)-2-benzoyl-3-phenyl-2-(prop-2-yn-1-yl)pent-4-enoate (3q).



3q

Ketoester **3q** was isolated by silica gel chromatography (2% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +57.7 (*c* 0.94, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.55 (m, 2H), 7.46 (ddt, *J* = 8.6, 7.0, 1.2 Hz, 1H), 7.35–7.29 (m, 2H), 7.25–7.23 (m, 5H), 6.37 (ddd, *J* = 17.0, 10.3, 7.8 Hz, 1H), 5.15 (ddd, *J* = 10.3, 1.8, 1.2 Hz, 1H), 5.09 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.58 (dt, *J* = 7.8, 1.3 Hz, 1H), 4.19–4.05 (m, 2H), 2.97 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.69 (dd, *J* = 17.4, 2.7 Hz, 1H), 2.09 (t, *J* = 2.7 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 171.4, 138.9, 137.6, 137.3, 132.5, 130.1, 128.4, 128.32, 128.27, 127.4, 117.6, 79.3, 72.9, 64.0, 61.7, 52.5, 25.7, 13.8; IR (Neat Film, NaCl) 3288, 3060, 3030, 2981, 1728, 1682, 1597, 1580, 1446, 1255, 1213, 1183, 1046, 1001, 925 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{23}H_{23}O_3$ $[M+H]^+$: 347.1642, found 347.1647; SFC conditions: 5% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): minor = 5.67, major = 6.44.

Ethyl (*E*)-2-benzoyl-5-phenyl-2-(prop-2-yn-1-yl)pent-4-enoate (4q).

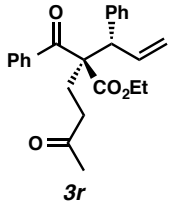


4q

Ketoester **4q** was isolated by silica gel chromatography (2% EtOAc in hexanes) as a colorless oil. 34% ee, $[\alpha]_D^{25}$ -23.4 (*c* 0.42, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88–7.85 (m, 2H), 7.59–7.54 (m, 1H), 7.48–7.42 (m, 2H), 7.30–7.24 (m, 4H), 7.21 (ddd, *J* = 8.7, 4.9, 3.8 Hz, 1H), 6.43 (dt, *J* = 15.6, 1.3 Hz, 1H), 5.90 (dt, *J* = 15.5, 7.7 Hz, 1H), 4.20 (qq, *J* = 7.1, 3.6 Hz, 2H), 3.19 (ddd, *J* = 14.5, 7.9, 1.3 Hz, 1H), 3.11 (ddd, *J* = 14.5, 7.5, 1.4 Hz, 1H), 2.98 (d, *J* = 2.7 Hz, 2H), 2.07 (t, *J* = 2.7 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 171.7, 137.1, 135.7, 134.9, 133.2, 128.8, 128.60, 128.57, 127.6, 126.4, 122.9, 79.0, 72.4, 62.1, 60.6, 36.5, 23.9, 14.1; IR (Neat Film, NaCl) 3287, 3059, 3026, 2979, 2933, 1729, 1679, 1596, 1580, 1446, 1367, 1285, 1270, 1239, 1192, 1180, 1094, 1064, 1023, 966, 937 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{23}H_{23}O_3$ $[M+H]^+$: 347.1642, found 347.1651; SFC

conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): minor = 9.81, major = 10.67.

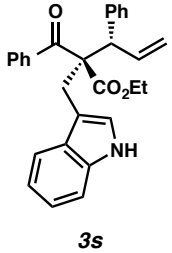
Ethyl (*R*)-2-benzoyl-5-oxo-2-((*S*)-1-phenylallyl)hexanoate (3r).



3r

Ketoester **3r** was isolated by silica gel chromatography (gradient elution, 5→10% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ +66.8 (*c* 1.20, $CHCl_3$); R_f = 0.4 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59–7.55 (m, 2H), 7.48–7.43 (m, 1H), 7.37–7.30 (m, 2H), 7.26–7.14 (m, 5H), 6.34 (ddd, *J* = 17.0, 10.3, 8.1 Hz, 1H), 5.09 (ddd, *J* = 10.3, 1.7, 1.0 Hz, 1H), 4.97 (ddd, *J* = 17.0, 1.7, 1.2 Hz, 1H), 4.36–4.32 (m, 1H), 4.13–3.99 (m, 2H), 2.46–2.38 (m, 1H), 2.34–2.29 (m, 2H), 2.25–2.17 (m, 1H), 1.99 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9, 198.0, 172.4, 139.1, 137.9, 137.8, 132.4, 129.7, 128.4, 128.3, 128.0, 127.3, 117.2, 64.2, 61.3, 53.2, 38.3, 29.9, 28.0, 13.7; IR (Neat Film, NaCl) 3063, 3030, 2981, 2905, 1733, 1717, 1681, 1637, 1596, 1582, 1495, 1446, 1419, 1367, 1243, 1214, 1137, 1093, 1029, 1002, 925, 860, 761 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{24}H_{27}O_3$ $[M+H]^+$: 379.1904, found 379.1911; SFC conditions: 5% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): minor = 8.00, major = 10.08.

Ethyl (2*R*,3*S*)-2-((1*H*-indol-3-yl)methyl)-2-benzoyl-3-phenylpent-4-enoate (3s).



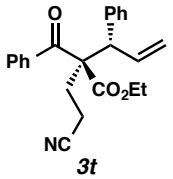
3s

Ketoester **3s** was isolated by silica gel chromatography (gradient elution, 5→10% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ –7.7 (*c* 1.60, $CHCl_3$); R_f = 0.4 (25% EtOAc in hexanes); ^{1}H NMR (300 MHz, C_6D_6) δ 7.70–7.65 (m, 1H), 7.36 (dd, *J* = 7.2,

1.8 Hz, 2H), 7.24–7.16 (m, 2H), 7.08–6.93 (m, 5H), 6.90–6.63 (m, 6H), 6.56 (br s, 1H), 5.17–5.12 (m, 1H), 5.10 (t, *J* = 1.0 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 3.82–3.63 (m, 3H), 3.62–3.45 (m, 1H), 0.40 (td, *J* = 6.7, 1.3 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 199.7, 172.2, 139.7, 139.6, 138.9, 135.5, 130.8, 130.2, 128.4, 128.1, 127.9, 127.8, 127.6, 126.9, 124.3, 121.6, 119.7, 119.2, 116.9, 110.5, 66.6, 60.4, 56.0, 31.9, 12.9; IR (Neat Film, NaCl) 3411, 3060, 1724, 1673, 1456, 1241, 1216, 1096, 1012, 923, 747 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{29}H_{28}NO_3$ $[M+H]^+$: 438.2064, found 438.2070; SFC conditions: 10% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): minor = 8.26, major = 9.30.

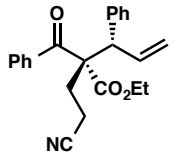
Ethyl (2*R*,3*S*)-2-benzoyl-2-(2-cyanoethyl)-3-phenylpent-4-enoate (3t) and ethyl (2*S*,3*S*)-2-benzoyl-2-(2-cyanoethyl)-3-phenylpent-4-enoate (3t').

Products **3t** and **3t'** were isolated by silica gel chromatography (5% EtOAc in hexanes) as a mixture of diastereomers (3:1), which were separated by preparative HPLC (20% EtOAc in hexanes).



3t
(major diastereomer)

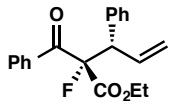
The major diastereomer was isolated as a white solid, >99% ee, $[\alpha]_D^{25}$ +59.1 (*c* 1.81, $CHCl_3$); R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.44 (m, 3H), 7.36–7.30 (m, 2H), 7.26–7.20 (m, 3H), 7.15–7.11 (m, 2H), 6.33 (ddd, *J* = 17.0, 10.2, 8.2 Hz, 1H), 5.14 (ddd, *J* = 10.2, 1.6, 1.0 Hz, 1H), 5.01 (dt, *J* = 17.0, 1.3 Hz, 1H), 4.32 (dt, *J* = 8.0, 1.0 Hz, 1H), 4.15–4.06 (m, 2H), 2.50–2.36 (m, 2H), 2.28 (td, *J* = 8.0, 0.8 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 171.8, 138.3, 137.5, 137.1, 132.8, 129.7, 128.7, 128.5, 128.1, 127.7, 119.1, 118.1, 64.0, 61.9, 53.6, 30.6, 13.7, 13.1; IR (Neat Film, NaCl) 3061, 3027, 2981, 2248, 1729, 1675, 1596, 1580, 1446, 1243, 1214, 1185, 1085, 1017, 971, 924, 757 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1751, found 362.1766; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 9.77, minor = 11.61.



3t′
(minor diastereomer)

The minor diastereomer was isolated as a white solid, >99% ee, $[\alpha]_D^{25}$ +22.3 (*c* 0.11, $CHCl_3$); R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.63 (m, 2H), 7.55–7.47 (m, 1H), 7.41–7.32 (m, 2H), 7.31–7.22 (m, 4H), 7.22–7.16 (m, 1H), 6.29 (dt, *J* = 16.8, 10.2 Hz, 1H), 5.21–5.11 (m, 2H), 4.35 (d, *J* = 10.3 Hz, 1H), 4.03 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.84 (dq, *J* = 10.8, 7.2 Hz, 1H), 2.74–2.63 (m, 1H), 2.46–2.28 (m, 2H), 2.14–2.02 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 171.3, 139.7, 136.7, 136.0, 133.0, 129.7, 128.7, 128.5, 128.3, 127.4, 119.2, 118.9, 63.8, 61.7, 53.0, 30.7, 13.3, 12.9; IR (Neat Film, NaCl) 3062, 3029, 2982, 2248, 1728, 1678, 1596, 1580, 1494, 1446, 1367, 1275, 1242, 1215, 1093, 1018, 972, 928, 757 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1751, found 362.1757; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 10.65, minor = 12.02.

Ethyl (2*S*,3*S*)-2-benzoyl-2-fluoro-3-phenylpent-4-enoate (3u).

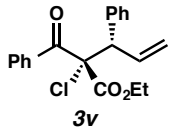


3u

Ketoester **3u** was isolated by silica gel chromatography (gradient elution, 1→2% EtOAc in hexanes) as a colorless oil. 95% ee, $[\alpha]_D^{25}$ +82.0 (*c* 1.19, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (ddt, *J* = 7.6, 2.0, 1.2 Hz, 2H), 7.49 (ddt, *J* = 7.7, 7.0, 1.3 Hz, 1H), 7.38–7.30 (m, 4H), 7.31–7.14 (m, 3H), 6.20 (ddd, *J* = 17.0, 10.2, 9.4 Hz, 1H), 5.27 (ddt, *J* = 17.0, 1.5, 0.8 Hz, 1H), 5.23 (ddd, *J* = 10.1, 1.5, 0.6 Hz, 1H), 4.65 (dd, *J* = 33.3 (J_{H-F}), 9.4 Hz, 1H), 4.31 (ddq, *J* = 39.5, 10.8, 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6 (d, *J* = 27.1 Hz), 166.3 (d, *J* = 26.4 Hz), 137.4, 134.9 (d, *J* = 3.5 Hz), 134.5 (d, *J* = 4.0 Hz), 133.6, 129.9 (d, *J* = 2.6 Hz), 129.5 (d, *J* = 6.7 Hz), 128.5, 128.4, 127.4, 119.1, 103.1 (d, *J* = 208.4 Hz), 63.1, 54.4 (d, *J* = 18.3 Hz), 14.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -169.39 (d, *J* = 33.2 Hz); IR (Neat Film,

NaCl) 3062, 3030, 2982, 2934, 1749, 1694, 1597, 1454, 1447, 1367, 1230, 1187, 1129, 1038, 929, 856, 743 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{20}H_{20}FO_3$ $[M+H]^+$: 327.1391, found 327.1401; SFC conditions: 5% IPA, 4.0 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 2.02, minor = 3.18.

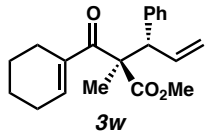
Ethyl (2*S*,3*S*)-2-benzoyl-2-chloro-3-phenylpent-4-enoate (3v).



3v

Ketoester **3v** was isolated by silica gel chromatography (gradient elution, 2→3% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +93.8 (*c* 1.43, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.54–7.47 (m, 1H), 7.47–7.40 (m, 2H), 7.40–7.33 (m, 2H), 7.33–7.18 (m, 3H), 6.36 (ddd, *J* = 16.9, 10.2, 8.7 Hz, 1H), 5.20 (ddd, *J* = 10.2, 1.5, 0.8 Hz, 1H), 5.15 (ddd, *J* = 16.9, 1.6, 1.0 Hz, 1H), 4.66 (d, *J* = 8.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.8, 167.3, 138.0, 135.9, 134.8, 133.1, 130.7, 129.3, 128.3, 128.0, 127.5, 118.7, 77.3, 63.4, 55.8, 13.8; IR (Neat Film, NaCl) 3062, 3029, 2982, 1754, 1696, 1597, 1581, 1446, 1367, 1299, 1239, 1207, 1186, 1094, 1075, 1025, 1007, 928, 749 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{20}H_{20}ClO_3$ $[M+H]^+$: 343.1095, found 343.1099; SFC conditions: 10% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 2.52, minor = 2.77.

Ethyl (2*R*,3*S*)-2-(cyclohex-1-ene-1-carbonyl)-2-methyl-3-phenylpent-4-enoate (3w).

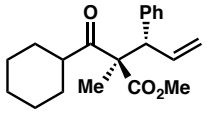


3w

Ketoester **3w** was isolated by silica gel chromatography (1% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ +80.8 (*c* 1.00, $CHCl_3$,); R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.13 (m, 5H), 6.47 (td, *J* = 3.9, 2.0 Hz, 1H), 6.25 (ddd, *J* = 16.8, 10.3, 8.0 Hz, 1H), 5.09 (dt, *J* = 10.2, 1.4 Hz, 1H), 5.00 (dt, *J* = 16.9, 1.4 Hz, 1H), 4.29 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.68 (d, *J* = 0.8 Hz, 3H), 2.24–2.03 (m, 3H),

1.97–1.81 (m, 1H), 1.55 (tq, J = 7.0, 4.0, 2.3 Hz, 4H), 1.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 173.8, 139.4, 138.3, 137.9, 137.2, 130.0, 128.0, 126.8, 117.1, 61.1, 54.5, 52.2, 25.9, 24.3, 22.0, 21.3, 20.7; IR (Neat Film, NaCl) 2938, 1732, 1671, 1636, 1452, 1433, 1234, 1113, 984, 917, 703 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found 313.1785; SFC conditions: 5% MeOH, 4.0 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): minor = 5.83, major = 6.55.

Methyl (2*R*,3*S*)-2-(cyclohexanecarbonyl)-2-methyl-3-phenylpent-4-enoate (3x).

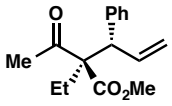


3x

Ketoester **3x** was isolated by silica gel chromatography (5% EtOAc in hexanes) as a mixture of diastereomers (4:1 dr). *For the major isomer*: 96% ee, $[\alpha]_D^{25}$ +57.7 (*c* 1.54, $CHCl_3$, measured with 4:1 dr mixture); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.18 (m, 5H), 6.26 (ddd, J = 17.0, 10.2, 8.5 Hz, 1H), 5.08 (ddd, J = 10.2, 1.8, 0.9 Hz, 1H), 5.00 (ddd, J = 17.0, 1.8, 1.1 Hz, 1H), 4.18 (dt, J = 8.5, 1.0 Hz, 1H), 3.71 (s, 3H), 2.50 (tt, J = 11.4, 3.2 Hz, 1H), 1.79–1.56 (m, 5H), 1.53–1.46 (m, 1H), 1.33 (s, 3H), 1.32–1.11 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.3, 172.4, 139.6, 137.8, 129.9, 128.3, 127.0, 117.4, 64.7, 54.1, 52.2, 48.4, 30.3, 29.6, 25.8, 25.73, 25.71, 18.7; IR (Neat Film, NaCl) 2933, 2854, 1729, 1708, 1635, 1495, 1453, 1432, 1380, 1315, 1228, 1144, 1101, 989, 919 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{20}H_{26}O_3$ $[M+H]^+$: 315.1955, found 315.1955; SFC conditions: 100% CO_2, 4.0 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): minor = 7.28, major = 7.96.

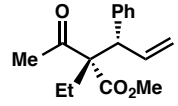
Methyl (2*R*,3*S*)-2-acetyl-2-ethyl-3-phenylpent-4-enoate (3y) and methyl (2*S*,3*S*)-2-acetyl-2-ethyl-3-phenylpent-4-enoate (3y').

Ketoesters **3y** and **3y'** were isolated by silica gel chromatography (gradient elution, 0→4% EtOAc in hexanes) as mixture of two diastereomers (1.5:1 dr). The diastereomers were separated by preparative HPLC (gradient elution, 60→70% MeCN in H_2O).



3y
major diastereomer

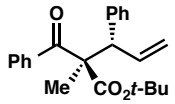
The major diastereomer was isolated as a colorless oil. 90% ee, $[\alpha]_D^{25}$ +72.7 (*c* 0.60, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.25–7.18 (m, 1H), 7.17–7.07 (m, 2H), 6.28 (ddd, *J* = 17.0, 10.2, 8.4 Hz, 1H), 5.08 (ddd, *J* = 10.2, 1.7, 0.9 Hz, 1H), 4.97 (ddd, *J* = 17.0, 1.7, 1.1 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H), 2.06 (s, 3H), 1.86–1.68 (m, 2H), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.8, 172.4, 139.5, 137.7, 129.3, 128.4, 127.3, 117.3, 68.2, 53.5, 51.9, 29.8, 27.4, 9.1; IR (Neat Film, NaCl) 3083, 3029, 2978, 2950, 2883, 1709, 1601, 1494, 1434, 1385, 1353, 1301, 1220, 1116, 1029, 993, 919, 755 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found 261.1492; SFC conditions: 0.5% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): minor = 4.79, major = 7.02.



3y′
minor diastereomer

The minor diastereomer was isolated as a colorless oil. 91% ee, $[\alpha]_D^{25}$ +25.3 (*c* 0.26, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.23 (m, 2H), 7.21–7.17 (m, 1H), 7.17–7.13 (m, 2H), 6.31 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.15 (ddd, *J* = 10.2, 1.6, 0.7 Hz, 1H), 5.10 (ddd, *J* = 17.0, 1.7, 1.0 Hz, 1H), 4.11 (d, *J* = 9.4 Hz, 1H), 3.63 (s, 3H), 2.12 (s, 3H), 2.09–1.98 (m, 1H), 1.80 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3, 172.3, 140.1, 137.3, 129.4, 128.2, 127.0, 117.6, 68.0, 52.5, 51.9, 30.1, 26.9, 8.8; IR (Neat Film, NaCl) 3063, 3030, 2962, 2925, 2850, 1710, 1600, 1446, 1354, 1286, 1260, 1223, 1182, 1118, 1095, 1023, 921, 864, 801 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{21}O_3$ $[M+H]^+$: 261.1485, found 261.1494; SFC conditions: 0.5% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): minor = 6.29, major = 7.02.

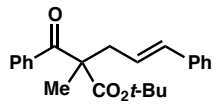
***tert*-Butyl (2*R*,3*S*)-2-benzoyl-2-methyl-3-phenylpent-4-enoate (3z).**



3z

Ketoester **3z** was isolated by silica gel chromatography (gradient elution, 0→2→5% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +67.4 (*c* 1.54, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.70 (m, 2H), 7.49–7.46 (m, 1H), 7.39–7.34 (m, 2H), 7.25–7.16 (m, 5H), 6.34 (ddd, *J* = 17.0, 10.3, 7.9 Hz, 1H), 5.12 (ddd, *J* = 10.3, 1.8, 1.1 Hz, 1H), 5.03 (dt, *J* = 17.0, 1.6 Hz, 1H), 4.42 (dt, *J* = 7.9, 1.2 Hz, 1H), 1.50 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 171.8, 139.7, 138.1, 137.3, 132.2, 130.4, 128.5, 128.3, 128.1, 126.9, 117.1, 82.6, 62.1, 54.6, 27.8, 21.0; IR (Neat Film, NaCl) 3061, 3027, 2978, 2934, 1728, 1716, 1687, 1682, 1598, 1454, 1446, 1251, 1155, 1115, 961, 918, 844 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{23}H_{27}O_3$ $[M+H]^+$: 351.1955, found 351.1955; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 4.14, minor = 5.80.

***tert*-Butyl (*E*)-2-benzoyl-2-methyl-5-phenylpent-4-enoate (4z).**

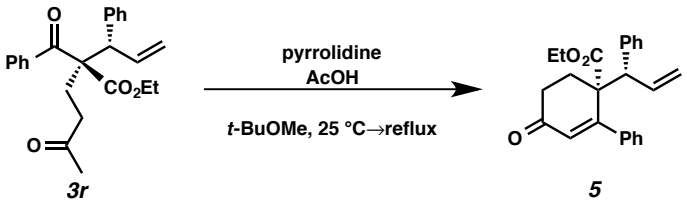


4z

Ketoester **4z** was isolated by silica gel chromatography (gradient elution, 0→2→5% EtOAc in hexanes) as a colorless oil. 38% ee, $[\alpha]_D^{25}$ +3.9 (*c* 0.74, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92–7.89 (m, 2H), 7.56–7.51 (m, 1H), 7.46–7.41 (m, 2H), 7.33–7.27 (m, 4H), 7.23–7.18 (m, 1H), 6.39 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.16–6.06 (m, 1H), 2.93 (ddd, *J* = 14.2, 7.5, 1.4 Hz, 1H), 2.84 (ddd, *J* = 14.2, 7.7, 1.3 Hz, 1H), 1.55 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.8, 172.8, 137.3, 135.9, 133.9, 132.7, 128.8, 128.6, 128.5, 127.4, 126.3, 124.7, 82.2, 58.0, 40.7, 27.8, 21.5; IR (Neat Film, NaCl) 3058, 3026, 2977, 2933, 1728, 1686, 1682, 1597, 1579, 1447, 1368, 1249, 1212, 1152, 1111, 970, 845 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{23}H_{27}O_3$ $[M+H]^+$: 351.1955, found 351.1949; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 9.88, minor = 8.48.

Procedures/Spectroscopic Data for Derivatization of Allylic Alkylation Products

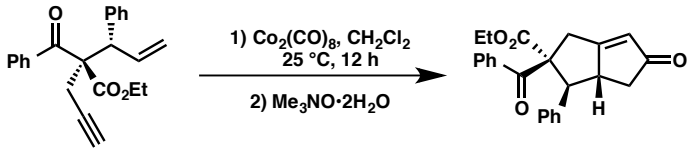
Synthesis of cyclohexenone 5:



3r *5*

To a solution of ketoester **3r** (60.4 mg, 0.6 mmol) in *t*-BuOMe (2 mL) was added pyrrolidine (13.7 mg, 0.19 mmol) and AcOH (11.6 mg, 0.19 mmol). The mixture was stirred for 12 h at 25 °C then heated to reflux for 4 h. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica gel (gradient elution, 10→25% EtOAc in hexanes) to give cyclohexenone **5** (55.1 mg, 95% yield) as a colorless oil. $[\alpha]_D^{25}$ +151.4 (*c* 1.19, $CHCl_3$); R_f = 0.5 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 1H), 7.25–7.19 (m, 2H), 7.13–7.04 (m, 3H), 7.04–6.97 (m, 2H), 6.69–6.63 (m, 2H), 6.33 (ddd, *J* = 16.9, 10.2, 7.8 Hz, 1H), 6.07 (s, 1H), 5.10 (ddd, *J* = 10.2, 1.6, 1.0 Hz, 1H), 4.87 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.26 (dt, *J* = 7.5, 1.5 Hz 1H), 2.91–2.77 (m, 1H), 2.62–2.53 (m, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5, 173.2, 161.6, 139.5, 139.2, 138.0, 131.9, 129.8, 128.7, 128.2, 128.1, 128.0, 126.7, 118.1, 62.0, 54.0, 53.8, 34.7, 30.9, 14.3; IR (Neat Film, NaCl) 3058, 3030, 2981, 1725, 1673, 1602, 1492, 1444, 1326, 1240, 1214, 1170, 1016, 921, 882 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{24}H_{25}O_3$ $[M+H]^+$: 361.1798, found 361.1798.

Synthesis of bicyclic enone 6:

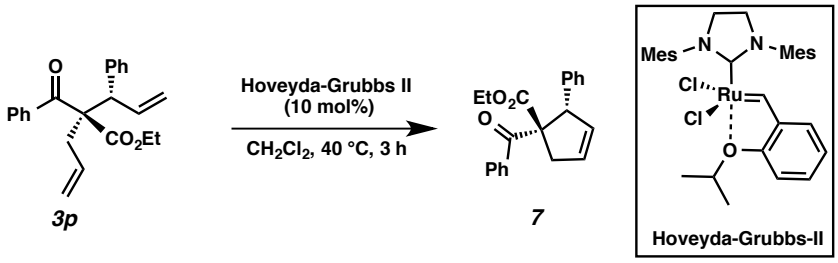


3q *6*

A dried flask was charged with a solution of enyne **3q** (8.6 mg, 0.025 mmol) and $Co_2(CO)_8$ (11.8 mg, 0.034 mmol) in CH_2Cl_2 (2 mL) and the mixture was stirred at room

temperature for 12 h under an atmosphere of argon. After full consumption of **3q** was observed by TLC analysis, $Me_3NO•2H_2O$ (7.6 mg, 0.068 mmol) was added. The mixture was stirred for 20 min and an additional portion of $Me_3NO•2H_2O$ (30.1 mg, 0.27 mmol) was added. Stirring was continued until complete consumption of the cobalt-alkyne complex was observed by TLC analysis (about 4 h). The mixture was filtered through a celite pad, washed with CH_2Cl_2, the solvent removed under reduced pressure, and the residue subjected to column chromatography on silica gel (25% EtOAc in hexanes) to give the bicyclic enone **6** (9.3 mg, 99% yield) as a colorless oil. The relative stereochemistry of **6** was assigned by 2D-NOESY. $[\alpha]_D^{25}$ -178.8 (*c* 0.79, $CHCl_3$); R_f = 0.3 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.26 (m, 1H), 7.26–7.18 (m, 4H), 7.13–7.02 (m, 5H), 6.03 (td, *J* = 2.2, 1.1 Hz, 1H), 4.11–3.91 (m, 3H), 3.82 (d, *J* = 12.3 Hz, 1H), 3.73–3.63 (m, 1H), 3.01 (dq, *J* = 18.2, 1.1 Hz, 1H), 2.54 (ddd, *J* = 18.0, 6.4, 0.8 Hz, 1H), 2.14 (ddd, *J* = 18.0, 2.5, 1.7 Hz, 1H), 0.86 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 197.1, 183.8, 173.3, 137.1, 136.7, 132.4, 129.5, 128.5, 128.3, 127.9, 127.8, 126.1, 68.6, 62.0, 55.8, 50.4, 41.7, 39.2, 13.6; IR (Neat Film, NaCl) 3034, 2979, 2927, 1733, 1714, 1668, 1636, 1600, 1583, 1449, 1409, 1255, 1211, 1183, 1071, 1043, 927, 914, 819 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{24}H_{23}O_4$ $[M+H]^+$: 375.1596, found 375.1592.

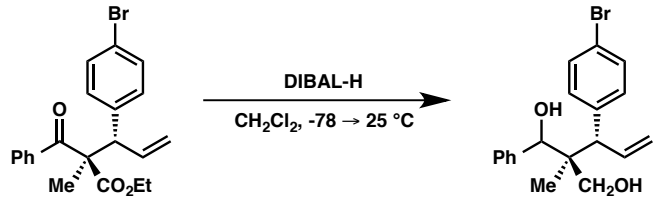
Synthesis of compound 7:



To a flame-dried Schlenk flask was added a solution of **3p** (20.8 mg, 0.06 mmol in 1.5 mL of CH_2Cl_2) and Hoveyda-Grubbs II catalyst (3.7 mg, 10 mol%). The reaction mixture was stirred for 3 h at 40 °C, filtered through a short silica pad and purified by silica gel chromatography (gradient elution, 1→5% EtOAc in hexanes) to give ketoester **7** (18.3 mg, 96% yield) as a white solid. $[\alpha]_D^{25}$ -613.7 (*c* 0.94, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61–7.55 (m, 2H), 7.38 (ddt, *J* = 8.6, 7.1, 1.2

Hz, 1H), 7.28–7.21 (m, 2H), 6.97–6.93 (m, 3H), 6.89–6.83 (m, 2H), 5.90 (ddt, *J* = 6.1, 2.6, 1.8 Hz, 1H), 5.75 (dtd, *J* = 5.5, 2.6, 1.5 Hz, 1H), 4.92 (q, *J* = 2.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.03 (dtd, *J* = 18.0, 2.6, 1.9 Hz, 1H), 2.73 (ddd, *J* = 18.0, 2.6, 1.6 Hz, 1H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 174.4, 138.4, 136.6, 133.8, 132.5, 129.5, 128.5, 128.1, 128.0, 127.4, 127.0, 68.3, 61.9, 58.0, 41.5, 13.8; IR (Neat Film, NaCl) 3060, 3028, 2959, 2932, 2871, 1736, 1732, 1686, 1682, 1598, 1582, 1492, 1447, 1365, 1258, 1243, 1220, 1157, 1087, 1048, 1004, 966, 922, 876, 761 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{21}O_3$ $[M+H]^+$: 321.1485, found 321.1489.

Determination of the Absolute Confirmation of Compound 3f



3f ***S-3f***

~ 1:1 dr mixture

To a flame-dried flask was added **3f** (98% ee, 62.1 mg, 0.16 mmol), CH_2Cl_2 (5 mL) and this solution was cooled to -78 °C. DIBAL-H (0.62 mL, 1.0 M solution in hexane) was added dropwise by syringe. The mixture was stirred for 2 h at -78 °C, then allowed to warm to 25 °C and stirred for an additional 12 h. The reaction was then cooled to 0 °C, and another 0.62 mL of DIBAL-H solution was added, followed by stirring at 25 °C for 3 h. The reaction mixture was then quenched with saturated aqueous Rochelle's salt (20 mL) and stirred for another 3 h. The aqueous layer was partitioned with a total of 100 mL of CH_2Cl_2 and the combined organic phases washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (gradient elution, 5→20% EtOAc in hexanes) to give 40.2 mg (72% yield) of **S-3f** as white solid mixture (1:1 dr). The diastereomers were separated by preparative HPLC (gradient elution, 60→90% MeCN in H_2O). *For isomer a*: white solid, $[\alpha]_D^{25}$ +58.9 (*c* 0.47, $CHCl_3$); R_f = 0.4 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.46–7.39 (m, 4H), 7.36–7.31 (m, 2H), 7.31–7.27 (m, 1H), 7.27–7.23 (m, 2H), 6.79 (dt, *J* = 16.9, 10.1 Hz, 1H), 5.20–5.10 (m, 2H), 5.07 (s, 1H), 3.67 (d, *J* = 10.1 Hz, 1H), 3.34 (d, *J* = 11.2 Hz, 1H), 3.11 (dd, *J* = 11.1, 0.7 Hz, 1H), 1.56 (br s, 2H), 0.72 (s,

3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 141.0, 140.4, 131.6, 131.4, 128.04, 128.79, 127.8, 120.5, 116.5, 76.0, 66.6, 55.8, 46.2, 15.3; IR (Neat Film, NaCl) 3423, 3070, 2969, 2923, 1486, 1452, 1403, 1342, 1074, 1012, 916, 827 cm^{-1}; HRMS (ESI+) *m/z* calc'd for fragment $C_{19}H_{18}Br$ $[M-H_4O_2+H]^+$: 325.0586, found 325.0585. *For isomer b*: white solid, $[\alpha]_D^{25}$ +53.4 (*c* 0.43, $CHCl_3$); R_f = 0.4 (24% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.45 (m, 2H), 7.35–7.27 (m, 5H), 7.25–7.20 (m, 2H), 6.30 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.35 (ddd, *J* = 16.8, 1.9, 0.8 Hz, 1H), 5.24 (ddd, *J* = 10.0, 1.9, 0.5 Hz, 1H), 4.39 (d, *J* = 10.0 Hz, 1H), 4.26 (s, 1H), 3.64 (d, *J* = 11.6 Hz, 1H), 3.51 (dd, *J* = 11.6, 1.8 Hz, 1H), 1.58 (br s, 2H), 0.48 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 140.2, 137.2, 131.7, 131.3, 128.02, 127.97, 127.8, 120.6, 118.3, 80.0, 65.6, 49.7, 44.5, 15.5; IR (Neat Film, NaCl) 3372, 2973, 2938, 2888, 1637, 1486, 1473, 1454, 1402, 1348, 1266, 1203, 1101, 1077, 1024, 1010, 921, 894, 831, 782 cm^{-1}; HRMS (ESI+) *m/z* calc'd for fragment $C_{19}H_{18}Br$ $[M-H_4O_2+H]^+$: 325.0586, found 325.0588.

Linear Free-Energy Relationship Charts

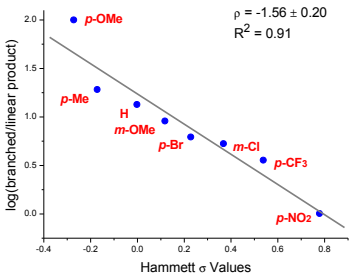


Figure 1. Linear relationship analysis of the log of product ratios (**3**:**4**) from Table 2 versus Hammett σ values.

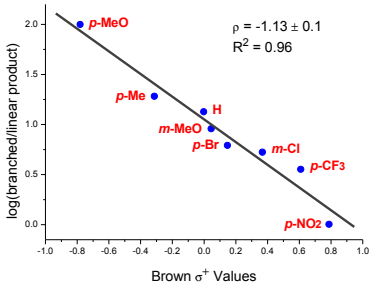
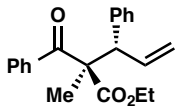
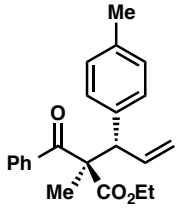
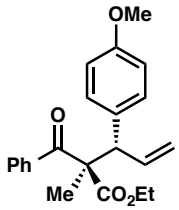
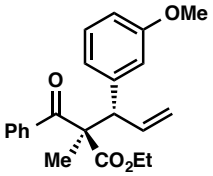
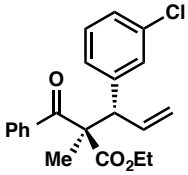
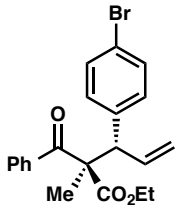
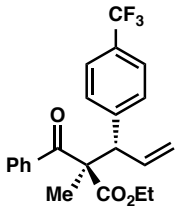
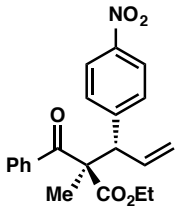
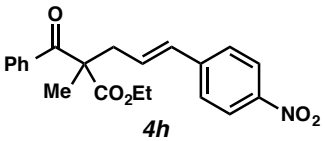
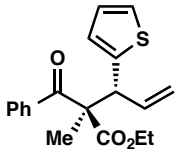
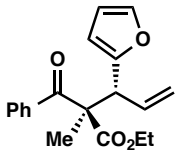
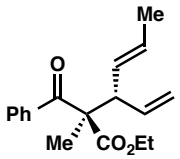
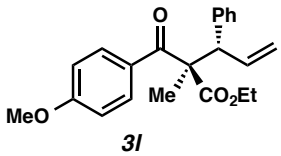
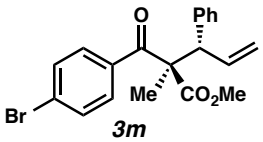
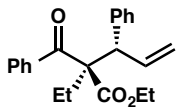
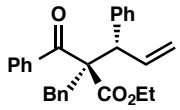
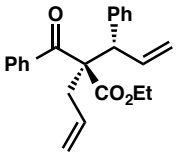
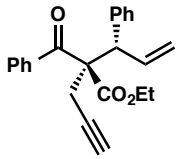
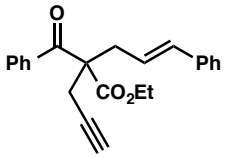
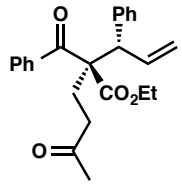
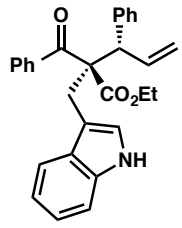
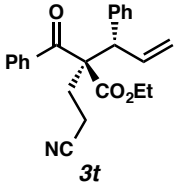


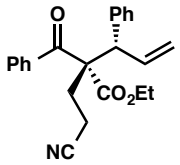
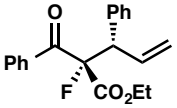
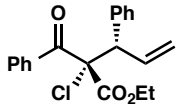
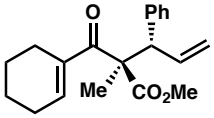
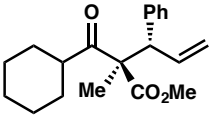
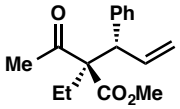
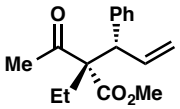
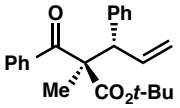
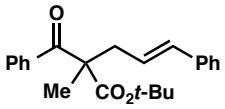
Figure 2. Linear relationship analysis of the log of product ratios (**3**:**4**) from Table 2 versus Brown σ^+ values.

Determination of Enantiomeric Excess (Table S2)

entry	compound	SFC analytic conditions	ee (%)
1	 ***3a***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 4.12, minor 6.14	98
2	 ***3b***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 6.71, minor 9.45	>99
3	 ***3c***	Chiralcel OJ-H, λ = 254 nm 4% IPA/CO_2, 2.5 mL/min t_R (min): minor 5.64, major 6.84	>99
4	 ***3d***	Chiralpak IC, λ = 254 nm 2% MeOH/CO_2, 2.5 mL/min t_R (min): major 12.24, minor 13.50	>99
5	 ***3e***	Chiralpak IC, λ = 254 nm 10% IPA/CO_2, 4.0 mL/min t_R (min): major 1.59, minor 1.77	99
6	 ***3f***	Chiralpak AD-H, λ = 254 nm 10% IPA/CO_2, 4.0 mL/min t_R (min): minor 2.95, major 3.17	>99

entry	compound	SFC analytic conditions	ee (%)
7	 ***3g***	**Chiralpak AD-H, λ = 254 nm 2% IPA/CO_2, 2.5 mL/min t_R (min): minor 5.20, major 6.68**	**>99**
8	 ***3h***	**Chiralpak AD-H, λ = 254 nm 5% MeOH/CO_2, 3.0 mL/min t_R (min): minor 4.47, major 5.71**	**93**
9	 ***4h***	**Chiralpak AD-H, λ = 254 nm 10% MeOH/CO_2, 3.0 mL/min t_R (min): major 7.13, minor 8.06**	**23**
10	 ***3i***	**Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 7.92, mino 11.24**	**95**
11	 ***3j***	**Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 5.09, minor 9.14**	**>99**
12	 ***3k***	**Chiralpak AD-H, λ = 210 nm 2% IPA/CO_2, 2.5 mL/min t_R (min): minor 4.40, major 5.52**	**91**
13	 ***3l***	**Chiralpak IC, λ = 254 nm 10% IPA/CO_2, 4.0 mL/min t_R (min): major 2.67, minor 3.51**	**99**
14	 ***3m***	**Chiralpak AD-H, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 5.35, minor = 5.88**	**>99**

entry	compound	SFC analytic conditions	ee (%)
15	 ***3n***	Chiralpak AD-H, λ = 254 nm, 5% MeOH/CO_2, 2.5 mL/min, t_R (min): major = 2.48, minor = 2.20	>99
16	 ***3o***	Chiralpak AD-H, λ = 254 nm 4% MeOH/CO_2, 4.0 mL/min t_R (min): major 5.06, minor 8.94	>99
17	 ***3p***	Chiralpak IC, λ = 254 nm 3% IPA/CO_2, 4.0 mL/min t_R (min): major 7.16, minor 8.60	>99
18	 ***3q***	Chiralcel OD-H, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): minor 5.67, major 6.44	>99
19	 ***4q***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 10.67, minor 9.81	34
20	 ***3r***	Chiralcel OD-H, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): minor 10.8, major 8.0	99
21	 ***3s***	Chiralpak IC, λ = 254 nm 10% MeOH/CO_2, 2.5 mL/min t_R (min): major 8.26, minor 9.30	>99
22	 ***3t***	Chiralpak AD-H, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 9.77, minor 11.60	>99

entry	compound	SFC analytic conditions	ee (%)
23	 ***3t'***	Chiralpak AD-H, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 10.65, minor 12.00	>99
24	 ***3u***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 4.0 mL/min t_R (min): major 2.02, minor 3.18	95
25	 ***3v***	Chiralpak IC, λ = 254 nm 10% IPA/CO_2, 2.5 mL/min t_R (min): major 2.52, minor 2.76	>99
26	 ***3w***	Chiralpak IC, λ = 254 nm 5% MeOH/CO_2, 4 mL/min t_R (min): major 6.56, minor 5.83	99
27	 ***3x***	Chiralcel OJ-H, λ = 210 nm 100% CO_2, 4.0 mL/min t_R (min): minor 7.28, major 7.96	96
28	 ***3y***	Chiralcel OJ-H, λ = 210 nm 0.5% IPA/CO_2, 2.5 mL/min t_R (min): minor 4.79, major 5.33	90
29	 ***3y'***	Chiralcel OJ-H, λ = 210 nm 0.5% IPA/CO_2, 2.5 mL/min t_R (min): minor 6.29, major 7.02	91
30	 ***3z***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 4.14, minor 5.80	>99
31	 ***4z***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min): major 9.88, minor 8.48	38

Crystal Structure Analysis of diol S-3f

The *mixture of diastereomers* **S-3f** were recrystallized from *i*-PrOH/heptane (liquid/liquid diffusion) to provide crystals suitable for X-ray analysis.

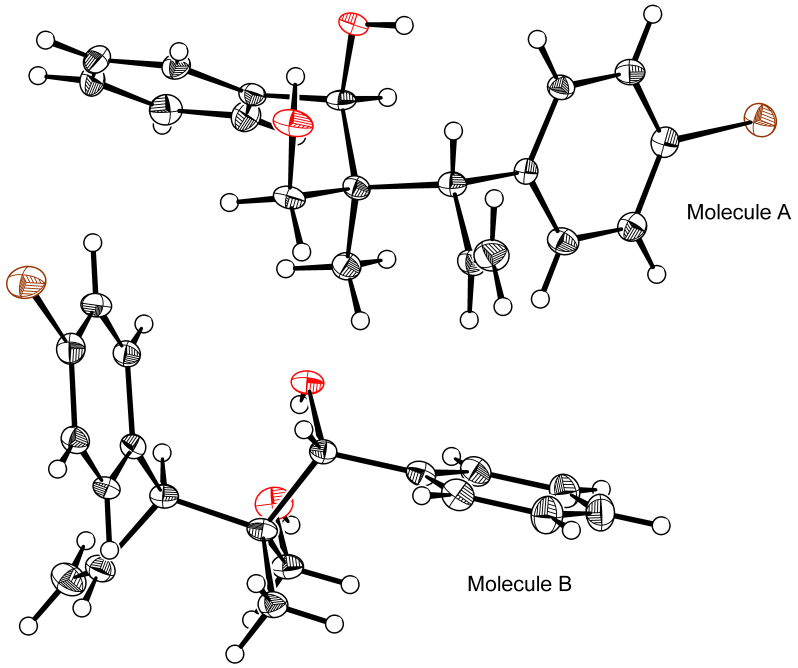


Table S3: Crystal Data and Structure Analysis Details for allylation diol S-3f (CCDC 959511).

Empirical formula	C19 H21 Br O2
Formula weight	361.27
Crystallization solvent	*i*-PrOH/heptane
Crystal shape	plate
Crystal color	colourless
Crystal size	0.06 x 0.16 x 0.45 mm

Data Collection

Preliminary photograph(s)	rotation
Type of diffractometer	Bruker APEX-II CCD
Wavelength	0.71073 Å MoK

Data collection temperature	100 K
Theta range for 9925 reflections used in lattice determination	2.31 to 24.19°
Unit cell dimensions	a = 11.871(3) Å ⟨= 90° b = 13.179(3) Å ®= 90° c = 21.761(5) Å © = 90°
Volume	3404.5(13) $Å^3$
Z	8
Crystal system	orthorhombic
Space group	P 21 21 21 (# 19)
Density (calculated)	1.410 g/cm^3
F(000)	1488
Theta range for data collection	1.8 to 32.3°
Completeness to theta = 25.000°	99.8%
Index ranges	-17 ″ h ″ 17, -19 ″ k ″ 19, -32 ″ l ″ 32
Data collection scan type	and scans
Reflections collected	88198
Independent reflections	11569 [R_{int}= 0.1174]
Reflections > 2 ∫(I)	8213
Average ∫(I)/(net I)	0.0905
Absorption coefficient	2.42 mm^{-1}
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6406

Structure Solution and Refinement

Primary solution method	dual
Secondary solution method	?
Hydrogen placement	geom
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11569 / 0 / 403
Treatment of hydrogen atoms	constr
Goodness-of-fit on F^2	1.31
Final R indices [I>2 ∫(I), 8213 reflections]	R1 = 0.0549, wR2 = 0.1052
R indices (all data)	R1 = 0.0967, wR2 = 0.1137
Type of weighting scheme used	calc
Weighting scheme used	w=1/[^2^(Fo^2^)+(0.0300P)^2^] where

P=(Fo^2^+2Fc^2^)/3	
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.032(5)
Extinction coefficient	n/a
Largest diff. peak and hole	1.70 and -0.98 e·Å^{-3}

Programs Used

Cell refinement	SAINT V8.32B (Bruker-AXS, 2007)
Data collection	APEX2 2013.6-2 (Bruker-AXS, 2007)
Data reduction	SAINT V8.32B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for CCDC 959511. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Br(1)	6018(1)	702(1)	2623(1)	24(1)
Br(1B)	2988(1)	6376(1)	6793(1)	29(1)
O(1)	2594(3)	2303(2)	5173(1)	17(1)
O(1B)	7801(3)	4619(2)	5244(2)	18(1)
O(2B)	9886(3)	5315(3)	5428(2)	24(1)
O(2)	1686(3)	4120(3)	5230(2)	24(1)
C(12)	4092(4)	2845(3)	5863(2)	16(1)
C(18)	2777(4)	4578(3)	5206(2)	18(1)
C(9)	3015(5)	4701(4)	3852(2)	18(1)
C(18B)	9487(4)	6230(4)	5137(2)	19(1)
C(8B)	6117(4)	7301(3)	6134(2)	17(1)
C(2B)	8002(4)	6397(4)	5956(2)	15(1)
C(1B)	8221(4)	6404(4)	5243(2)	16(1)
C(1)	3608(4)	3879(3)	4879(2)	15(1)
C(15)	4893(5)	2837(4)	7069(2)	24(1)
C(14)	3765(4)	3049(4)	6953(2)	22(1)
C(11)	3668(4)	2816(4)	5202(2)	16(1)
C(6)	5187(4)	1642(4)	3110(2)	18(1)
C(17)	5219(4)	2643(4)	5991(2)	21(1)
C(2)	3195(4)	3711(4)	4194(2)	16(1)
C(7B)	4982(4)	7302(4)	6324(2)	18(1)
C(8)	4928(4)	3307(4)	3522(2)	20(1)
C(3)	3933(4)	2995(3)	3819(2)	14(1)
C(13)	3366(4)	3055(4)	6356(2)	17(1)
C(19B)	7923(4)	7429(4)	4952(2)	19(1)

C(12B)	7652(4)	5450(4)	4243(2)	18(1)
C(6B)	4508(4)	6393(4)	6517(2)	21(1)
C(19)	4775(4)	4374(4)	4898(2)	20(1)
C(16)	5615(4)	2644(4)	6592(2)	22(1)
C(11B)	7514(4)	5552(3)	4936(2)	15(1)
C(4)	3595(4)	1989(4)	3747(2)	16(1)
C(5)	4218(4)	1308(4)	3397(2)	19(1)
C(3B)	6758(4)	6422(4)	6135(2)	15(1)
C(9B)	8651(4)	7213(4)	6288(2)	21(1)
C(7)	5550(4)	2637(4)	3168(2)	19(1)
C(13B)	8529(4)	4866(4)	3986(2)	22(1)
C(14B)	8635(5)	4779(4)	3355(2)	25(1)
C(4B)	6236(4)	5523(4)	6338(2)	18(1)
C(10B)	9604(4)	7033(4)	6590(2)	27(1)
C(10)	2036(5)	4974(4)	3618(2)	27(1)
C(15B)	7867(5)	5270(4)	2970(2)	28(1)
C(17B)	6896(4)	5927(4)	3852(2)	22(1)
C(5B)	5122(4)	5503(4)	6526(2)	21(1)
C(16B)	7008(5)	5844(4)	3217(2)	28(1)

Table S5. Bond lengths [Å] and angles [°] for CCDC 959511.

Br(1)-C(6)	1.906(5)
Br(1B)-C(6B)	1.902(5)
O(1)-H(1)	0.8400
O(1)-C(11)	1.445(5)
O(1B)-H(1B)	0.8400
O(1B)-C(11B)	1.443(5)
O(2B)-H(2B)	0.8400
O(2B)-C(18B)	1.442(6)
O(2)-H(2)	0.8400
O(2)-C(18)	1.430(5)
C(12)-C(11)	1.525(6)
C(12)-C(17)	1.391(7)
C(12)-C(13)	1.404(6)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(18)-C(1)	1.527(6)
C(9)-H(9)	0.9500
C(9)-C(2)	1.517(6)
C(9)-C(10)	1.319(7)
C(18B)-H(18C)	0.9900
C(18B)-H(18D)	0.9900
C(18B)-C(1B)	1.538(6)
C(8B)-H(8B)	0.9500
C(8B)-C(7B)	1.409(7)
C(8B)-C(3B)	1.386(7)
C(2B)-H(2BA)	1.0000
C(2B)-C(1B)	1.574(6)
C(2B)-C(3B)	1.527(6)
C(2B)-C(9B)	1.507(7)
C(1B)-C(19B)	1.532(6)

C(1B)-C(11B)	1.553(6)
C(1)-C(11)	1.568(6)
C(1)-C(2)	1.585(6)
C(1)-C(19)	1.531(6)
C(15)-H(15)	0.9500
C(15)-C(14)	1.391(7)
C(15)-C(16)	1.369(7)
C(14)-H(14)	0.9500
C(14)-C(13)	1.382(7)
C(11)-H(11)	1.0000
C(6)-C(5)	1.381(7)
C(6)-C(7)	1.386(7)
C(17)-H(17)	0.9500
C(17)-C(16)	1.391(6)
C(2)-H(2A)	1.0000
C(2)-C(3)	1.524(6)
C(7B)-H(7B)	0.9500
C(7B)-C(6B)	1.389(7)
C(8)-H(8)	0.9500
C(8)-C(3)	1.408(6)
C(8)-C(7)	1.385(7)
C(3)-C(4)	1.394(7)
C(13)-H(13)	0.9500
C(19B)-H(19D)	0.9800
C(19B)-H(19E)	0.9800
C(19B)-H(19F)	0.9800
C(12B)-C(11B)	1.522(6)
C(12B)-C(13B)	1.411(7)
C(12B)-C(17B)	1.387(7)
C(6B)-C(5B)	1.381(7)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(16)-H(16)	0.9500
C(11B)-H(11B)	1.0000
C(4)-H(4)	0.9500
C(4)-C(5)	1.391(7)
C(5)-H(5)	0.9500
C(3B)-C(4B)	1.408(7)
C(9B)-H(9B)	0.9500
C(9B)-C(10B)	1.329(7)
C(7)-H(7)	0.9500
C(13B)-H(13B)	0.9500
C(13B)-C(14B)	1.384(7)
C(14B)-H(14B)	0.9500
C(14B)-C(15B)	1.398(8)
C(4B)-H(4B)	0.9500
C(4B)-C(5B)	1.385(7)
C(10B)-H(10C)	0.9500
C(10B)-H(10D)	0.9500
C(10)-H(10A)	0.9500
C(10)-H(10B)	0.9500
C(15B)-H(15B)	0.9500
C(15B)-C(16B)	1.379(8)

C(17B)-H(17B)	0.9500
C(17B)-C(16B)	1.392(7)
C(5B)-H(5B)	0.9500
C(16B)-H(16B)	0.9500

C(11)-O(1)-H(1)	109.5
C(11B)-O(1B)-H(1B)	109.5
C(18B)-O(2B)-H(2B)	109.5
C(18)-O(2)-H(2)	109.5
C(17)-C(12)-C(11)	120.1(4)
C(17)-C(12)-C(13)	118.4(4)
C(13)-C(12)-C(11)	121.5(4)
O(2)-C(18)-H(18A)	109.6
O(2)-C(18)-H(18B)	109.6
O(2)-C(18)-C(1)	110.3(4)
H(18A)-C(18)-H(18B)	108.1
C(1)-C(18)-H(18A)	109.6
C(1)-C(18)-H(18B)	109.6
C(2)-C(9)-H(9)	118.4
C(10)-C(9)-H(9)	118.4
C(10)-C(9)-C(2)	123.3(5)
O(2B)-C(18B)-H(18C)	109.1
O(2B)-C(18B)-H(18D)	109.1
O(2B)-C(18B)-C(1B)	112.3(4)
H(18C)-C(18B)-H(18D)	107.9
C(1B)-C(18B)-H(18C)	109.1
C(1B)-C(18B)-H(18D)	109.1
C(7B)-C(8B)-H(8B)	119.2
C(3B)-C(8B)-H(8B)	119.2
C(3B)-C(8B)-C(7B)	121.7(4)
C(1B)-C(2B)-H(2BA)	106.1
C(3B)-C(2B)-H(2BA)	106.1
C(3B)-C(2B)-C(1B)	114.3(3)
C(9B)-C(2B)-H(2BA)	106.1
C(9B)-C(2B)-C(1B)	112.5(4)
C(9B)-C(2B)-C(3B)	110.9(4)
C(18B)-C(1B)-C(2B)	108.0(4)
C(18B)-C(1B)-C(11B)	110.8(4)
C(19B)-C(1B)-C(18B)	107.2(4)
C(19B)-C(1B)-C(2B)	112.0(4)
C(19B)-C(1B)-C(11B)	109.6(4)
C(11B)-C(1B)-C(2B)	109.3(4)
C(18)-C(1)-C(11)	111.0(4)
C(18)-C(1)-C(2)	108.8(4)
C(18)-C(1)-C(19)	108.3(4)
C(11)-C(1)-C(2)	108.1(4)
C(19)-C(1)-C(11)	109.2(4)
C(19)-C(1)-C(2)	111.4(4)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(16)-C(15)-C(14)	120.2(4)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-C(15)	120.1(4)
C(13)-C(14)-H(14)	120.0

O(1)-C(11)-C(12)	110.2(4)
O(1)-C(11)-C(1)	111.0(3)
O(1)-C(11)-H(11)	106.9
C(12)-C(11)-C(1)	114.5(4)
C(12)-C(11)-H(11)	106.9
C(1)-C(11)-H(11)	106.9
C(5)-C(6)-Br(1)	118.3(4)
C(5)-C(6)-C(7)	121.3(4)
C(7)-C(6)-Br(1)	120.4(4)
C(12)-C(17)-H(17)	119.6
C(12)-C(17)-C(16)	120.8(4)
C(16)-C(17)-H(17)	119.6
C(9)-C(2)-C(1)	112.6(4)
C(9)-C(2)-H(2A)	106.2
C(9)-C(2)-C(3)	110.5(4)
C(1)-C(2)-H(2A)	106.2
C(3)-C(2)-C(1)	114.3(4)
C(3)-C(2)-H(2A)	106.2
C(8B)-C(7B)-H(7B)	120.8
C(6B)-C(7B)-C(8B)	118.4(4)
C(6B)-C(7B)-H(7B)	120.8
C(3)-C(8)-H(8)	119.4
C(7)-C(8)-H(8)	119.4
C(7)-C(8)-C(3)	121.1(4)
C(8)-C(3)-C(2)	123.2(4)
C(4)-C(3)-C(2)	118.9(4)
C(4)-C(3)-C(8)	117.8(4)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-C(12)	120.4(4)
C(14)-C(13)-H(13)	119.8
C(1B)-C(19B)-H(19D)	109.5
C(1B)-C(19B)-H(19E)	109.5
C(1B)-C(19B)-H(19F)	109.5
H(19D)-C(19B)-H(19E)	109.5
H(19D)-C(19B)-H(19F)	109.5
H(19E)-C(19B)-H(19F)	109.5
C(13B)-C(12B)-C(11B)	121.4(4)
C(17B)-C(12B)-C(11B)	119.9(4)
C(17B)-C(12B)-C(13B)	118.8(4)
C(7B)-C(6B)-Br(1B)	119.3(4)
C(5B)-C(6B)-Br(1B)	119.1(4)
C(5B)-C(6B)-C(7B)	121.6(4)
C(1)-C(19)-H(19A)	109.5
C(1)-C(19)-H(19B)	109.5
C(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(15)-C(16)-C(17)	120.1(5)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
O(1B)-C(11B)-C(1B)	106.8(3)
O(1B)-C(11B)-C(12B)	111.1(4)
O(1B)-C(11B)-H(11B)	107.7

C(1B)-C(11B)-H(11B)	107.7
C(12B)-C(11B)-C(1B)	115.5(4)
C(12B)-C(11B)-H(11B)	107.7
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-C(3)	121.5(4)
C(5)-C(4)-H(4)	119.2
C(6)-C(5)-C(4)	119.0(5)
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-H(5)	120.5
C(8B)-C(3B)-C(2B)	123.3(4)
C(8B)-C(3B)-C(4B)	117.5(4)
C(4B)-C(3B)-C(2B)	119.2(4)
C(2B)-C(9B)-H(9B)	118.5
C(10B)-C(9B)-C(2B)	123.0(5)
C(10B)-C(9B)-H(9B)	118.5
C(6)-C(7)-H(7)	120.4
C(8)-C(7)-C(6)	119.2(4)
C(8)-C(7)-H(7)	120.4
C(12B)-C(13B)-H(13B)	119.8
C(14B)-C(13B)-C(12B)	120.4(5)
C(14B)-C(13B)-H(13B)	119.8
C(13B)-C(14B)-H(14B)	120.1
C(13B)-C(14B)-C(15B)	119.8(5)
C(15B)-C(14B)-H(14B)	120.1
C(3B)-C(4B)-H(4B)	119.0
C(5B)-C(4B)-C(3B)	122.0(4)
C(5B)-C(4B)-H(4B)	119.0
C(9B)-C(10B)-H(10C)	120.0
C(9B)-C(10B)-H(10D)	120.0
H(10C)-C(10B)-H(10D)	120.0
C(9)-C(10)-H(10A)	120.0
C(9)-C(10)-H(10B)	120.0
H(10A)-C(10)-H(10B)	120.0
C(14B)-C(15B)-H(15B)	119.9
C(16B)-C(15B)-C(14B)	120.2(5)
C(16B)-C(15B)-H(15B)	119.9
C(12B)-C(17B)-H(17B)	119.6
C(12B)-C(17B)-C(16B)	120.8(5)
C(16B)-C(17B)-H(17B)	119.6
C(6B)-C(5B)-C(4B)	118.9(5)
C(6B)-C(5B)-H(5B)	120.6
C(4B)-C(5B)-H(5B)	120.6
C(15B)-C(16B)-C(17B)	120.1(5)
C(15B)-C(16B)-H(16B)	120.0
C(17B)-C(16B)-H(16B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for CCDC 959511. The anisotropic displacement factor exponent takes the form $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	216(2)	209(2)	285(2)	-37(2)	36(2)	57(2)
Br(1B)	176(2)	307(3)	382(3)	10(2)	76(2)	-18(2)
O(1)	164(16)	123(16)	218(17)	-4(14)	-13(13)	-28(13)
O(1B)	158(17)	130(16)	254(17)	27(13)	-4(14)	-4(13)
O(2B)	144(17)	223(19)	340(20)	29(15)	19(15)	75(15)
O(2)	149(16)	138(18)	430(20)	-13(16)	45(15)	28(13)
C(12)	160(20)	120(20)	190(20)	-7(17)	17(18)	-13(19)
C(18)	140(20)	120(20)	260(20)	-3(18)	8(18)	-9(17)
C(9)	240(20)	120(20)	200(20)	-3(17)	-10(20)	0(20)
C(18B)	160(20)	150(20)	260(20)	20(20)	33(18)	-3(19)
C(8B)	200(20)	110(20)	190(20)	-5(17)	5(19)	-20(20)
C(2B)	131(19)	120(20)	200(20)	15(18)	-1(18)	20(20)
C(1B)	150(20)	110(20)	220(20)	21(19)	-13(17)	0(18)
C(1)	150(20)	120(20)	190(20)	-8(17)	0(17)	8(17)
C(15)	360(30)	220(30)	130(20)	13(19)	-30(20)	-30(20)
C(14)	270(30)	200(20)	170(20)	11(18)	60(19)	-20(20)
C(11)	120(20)	130(20)	210(20)	20(18)	20(17)	-36(17)
C(6)	170(20)	190(20)	180(20)	10(18)	-5(18)	56(18)
C(17)	180(20)	240(30)	210(20)	10(20)	16(19)	10(20)
C(2)	140(20)	140(20)	200(20)	10(18)	6(17)	13(18)
C(7B)	180(20)	150(20)	210(20)	-17(18)	11(19)	20(20)
C(8)	150(20)	190(20)	250(20)	-13(19)	-1(19)	-20(19)
C(3)	140(20)	150(20)	136(19)	-1(16)	-2(17)	15(19)
C(13)	140(20)	190(20)	200(20)	5(19)	37(18)	-7(19)
C(19B)	200(20)	140(20)	230(20)	-3(18)	40(20)	10(20)
C(12B)	180(20)	140(20)	220(20)	5(18)	-18(18)	-6(18)
C(6B)	170(20)	250(30)	200(20)	-10(20)	3(18)	0(20)
C(19)	170(20)	240(30)	200(20)	0(20)	-18(17)	-60(20)
C(16)	200(20)	230(30)	240(30)	30(20)	-33(19)	10(20)
C(11B)	150(20)	130(20)	170(20)	20(17)	-14(17)	10(18)
C(4)	150(20)	160(20)	180(20)	0(18)	-5(17)	-22(18)
C(5)	210(20)	140(20)	210(20)	21(18)	0(17)	0(20)
C(3B)	150(20)	140(20)	160(20)	-4(18)	-8(16)	-5(18)
C(9B)	190(20)	190(20)	240(20)	-40(20)	31(19)	-40(20)
C(7)	150(20)	220(20)	200(20)	0(20)	13(19)	3(19)
C(13B)	230(30)	170(20)	240(30)	-20(20)	0(20)	20(20)
C(14B)	260(30)	220(30)	260(30)	-50(20)	40(20)	40(20)
C(4B)	210(30)	140(20)	180(20)	2(17)	0(18)	10(19)
C(10B)	210(30)	260(30)	330(30)	-50(20)	-10(20)	-20(20)
C(10)	330(30)	200(30)	280(30)	40(20)	-30(20)	20(30)
C(15B)	310(30)	330(30)	220(20)	-50(20)	20(20)	-10(30)
C(17B)	190(20)	200(30)	270(20)	-9(19)	-20(20)	40(20)
C(5B)	230(30)	160(30)	240(20)	0(19)	30(20)	-50(20)
C(16B)	280(30)	310(30)	230(20)	10(20)	-30(20)	40(20)

Table S7. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for CCDC 959511.

	x	y	z	U_{iso}

H(1)	239	225	480	25
H(1B)	849	462	533	27
H(2B)	1057	523	535	36
H(2)	175	351	533	36
H(18A)	304	472	563	21
H(18B)	273	523	498	21
H(9)	364	515	380	22
H(18C)	963	619	469	23
H(18D)	991	682	530	23
H(8B)	645	792	600	20
H(2BA)	830	574	611	18
H(15)	516	283	748	28
H(14)	327	319	728	26
H(11)	422	240	496	19
H(17)	572	250	566	25
H(2A)	244	338	422	19
H(7B)	455	791	632	22
H(8)	518	399	356	24
H(13)	260	320	628	21
H(19D)	838	796	514	29
H(19E)	712	757	502	29
H(19F)	808	740	451	29
H(19A)	476	502	467	30
H(19B)	533	392	471	30
H(19C)	499	451	533	30
H(16)	639	251	667	27
H(11B)	670	570	502	18
H(4)	292	176	394	20
H(5)	398	62	336	23
H(9B)	837	789	628	25
H(7)	622	286	297	23
H(13B)	905	453	425	26
H(14B)	923	439	318	30
H(4B)	666	491	635	21
H(10C)	990	637	660	32
H(10D)	998	757	679	32
H(10A)	140	454	366	32
H(10B)	197	560	341	32
H(15B)	794	521	254	34
H(17B)	630	632	402	26
H(5B)	479	489	666	25
H(16B)	649	618	295	33

Table S8. Hydrogen bonds for CCDC 959511 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1B)-H(1B)...O(2B)	0.84	1.91	2.669(5)	150.6
O(2B)-H(2B)...O(2)#1	0.84	1.99	2.689(5)	140.2

O(2)-H(2)...O(1)	0.84	1.91	2.629(5)	142.7

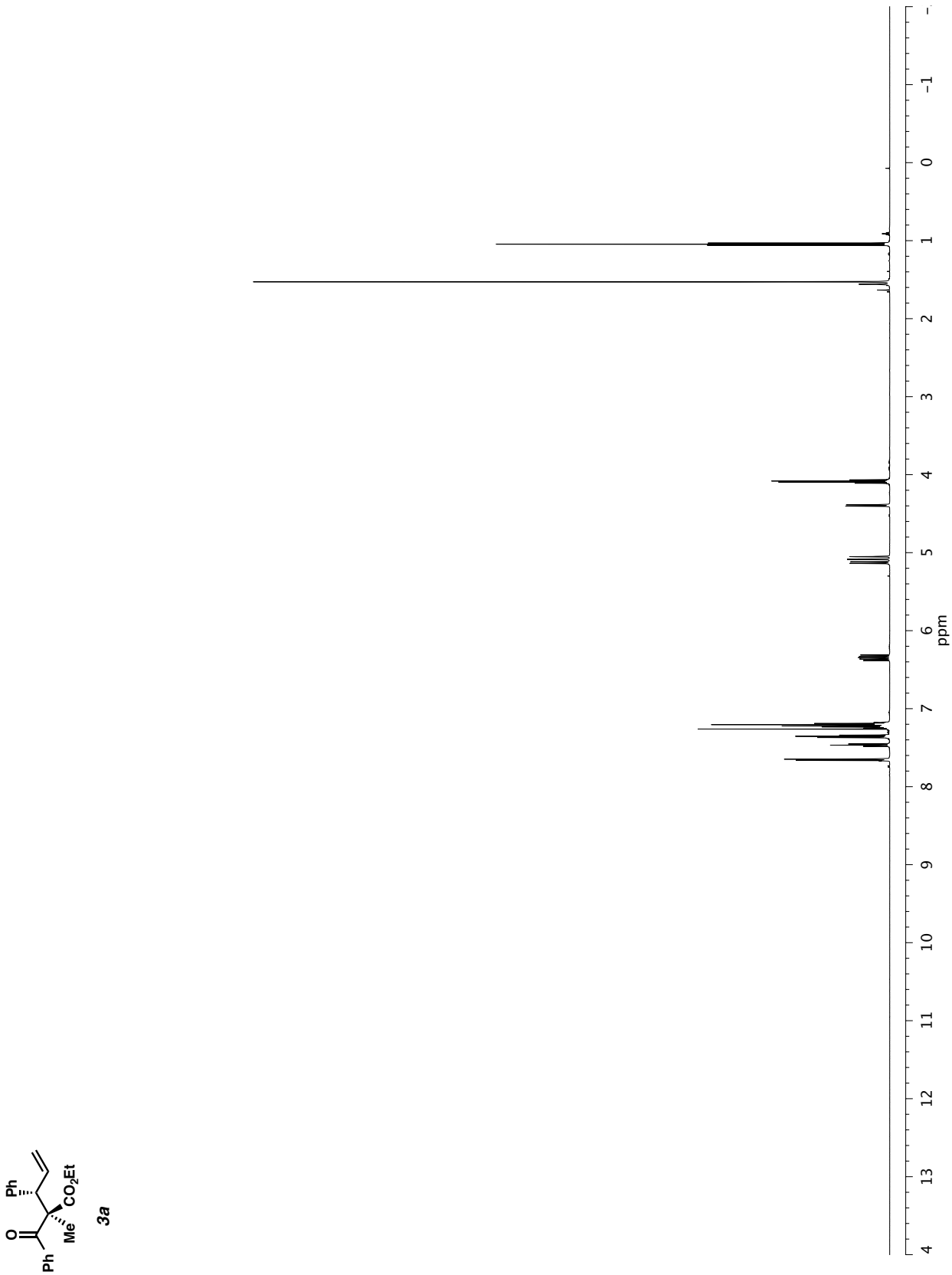
Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z

Table S9. Torsion angles [°] for CCDC 959511.

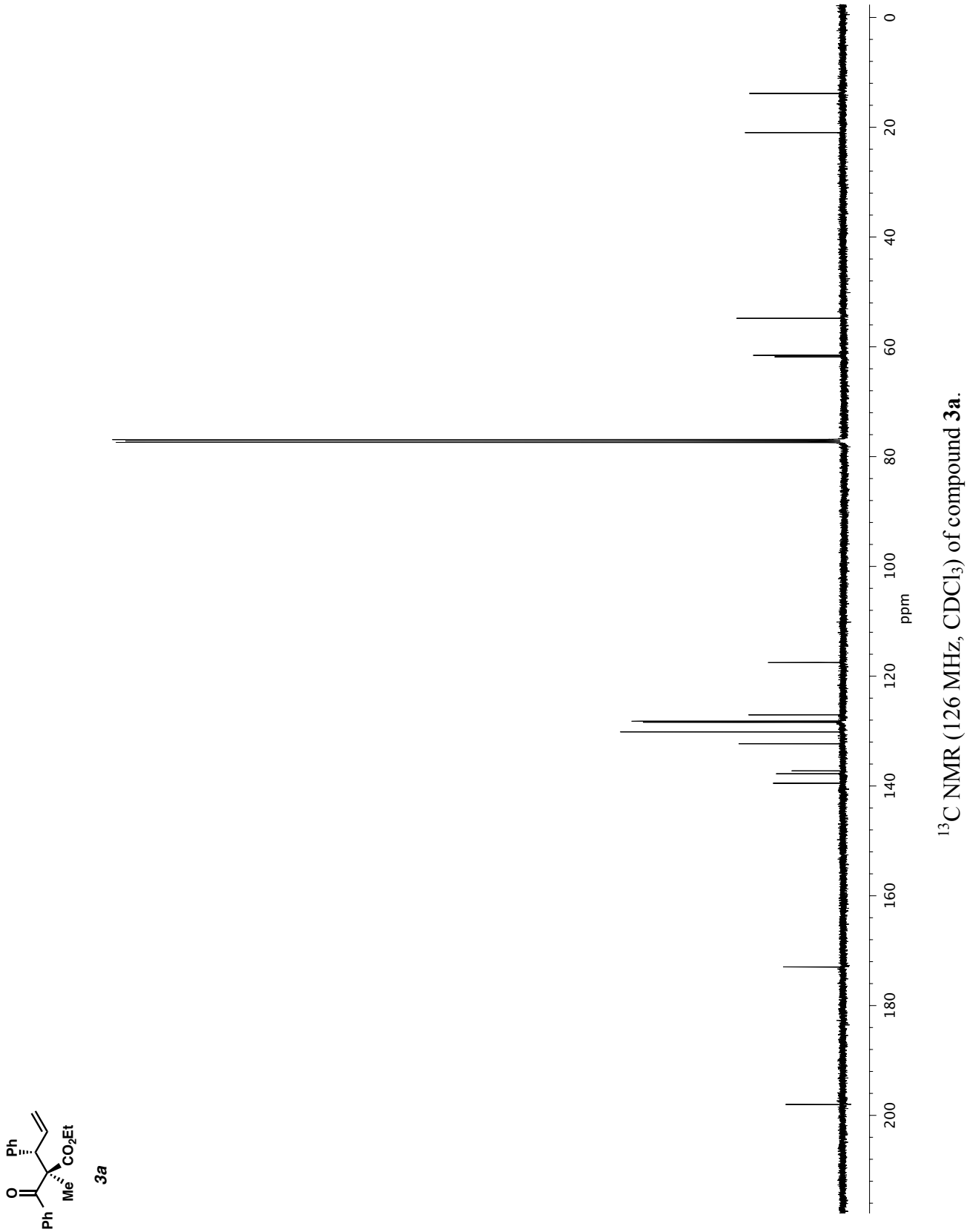
Br(1)-C(6)-C(5)-C(4)	-179.3(3)
Br(1)-C(6)-C(7)-C(8)	179.6(3)
Br(1B)-C(6B)-C(5B)-C(4B)	-178.6(3)
O(2B)-C(18B)-C(1B)-C(2B)	55.2(5)
O(2B)-C(18B)-C(1B)-C(19B)	176.0(4)
O(2B)-C(18B)-C(1B)-C(11B)	-64.4(5)
O(2)-C(18)-C(1)-C(11)	-57.0(5)
O(2)-C(18)-C(1)-C(2)	61.9(5)
O(2)-C(18)-C(1)-C(19)	-176.9(4)
C(12)-C(17)-C(16)-C(15)	0.5(8)
C(18)-C(1)-C(11)-O(1)	63.0(5)
C(18)-C(1)-C(11)-C(12)	-62.6(5)
C(18)-C(1)-C(2)-C(9)	54.6(5)
C(18)-C(1)-C(2)-C(3)	-178.1(4)
C(9)-C(2)-C(3)-C(8)	45.4(6)
C(9)-C(2)-C(3)-C(4)	-132.4(4)
C(18B)-C(1B)-C(11B)-O(1B)	64.1(5)
C(18B)-C(1B)-C(11B)-C(12B)	-60.1(5)
C(8B)-C(7B)-C(6B)-Br(1B)	178.6(3)
C(8B)-C(7B)-C(6B)-C(5B)	0.0(7)
C(8B)-C(3B)-C(4B)-C(5B)	0.6(7)
C(2B)-C(1B)-C(11B)-O(1B)	-54.8(5)
C(2B)-C(1B)-C(11B)-C(12B)	-179.0(4)
C(2B)-C(3B)-C(4B)-C(5B)	177.8(4)
C(1B)-C(2B)-C(3B)-C(8B)	-79.4(5)
C(1B)-C(2B)-C(3B)-C(4B)	103.6(5)
C(1B)-C(2B)-C(9B)-C(10B)	-100.3(5)
C(1)-C(2)-C(3)-C(8)	-83.0(5)
C(1)-C(2)-C(3)-C(4)	99.3(5)
C(15)-C(14)-C(13)-C(12)	0.1(7)
C(14)-C(15)-C(16)-C(17)	-1.0(8)
C(11)-C(12)-C(17)-C(16)	-178.5(4)
C(11)-C(12)-C(13)-C(14)	178.2(4)
C(11)-C(1)-C(2)-C(9)	175.3(4)
C(11)-C(1)-C(2)-C(3)	-57.4(5)
C(17)-C(12)-C(11)-O(1)	137.1(4)
C(17)-C(12)-C(11)-C(1)	-97.0(5)
C(17)-C(12)-C(13)-C(14)	-0.6(7)
C(2)-C(1)-C(11)-O(1)	-56.4(5)
C(2)-C(1)-C(11)-C(12)	178.1(4)
C(2)-C(3)-C(4)-C(5)	178.2(4)
C(7B)-C(8B)-C(3B)-C(2B)	-177.6(4)
C(7B)-C(8B)-C(3B)-C(4B)	-0.6(6)
C(7B)-C(6B)-C(5B)-C(4B)	0.0(7)
C(8)-C(3)-C(4)-C(5)	0.3(7)
C(3)-C(8)-C(7)-C(6)	-0.2(7)
C(3)-C(4)-C(5)-C(6)	-0.6(7)
C(13)-C(12)-C(11)-O(1)	-41.8(6)
C(13)-C(12)-C(11)-C(1)	84.2(5)
C(13)-C(12)-C(17)-C(16)	0.3(7)
C(19B)-C(1B)-C(11B)-O(1B)	-177.8(3)

C(19B)-C(1B)-C(11B)-C(12B)	58.0(5)
C(12B)-C(13B)-C(14B)-C(15B)	-0.1(8)
C(12B)-C(17B)-C(16B)-C(15B)	1.0(8)
C(19)-C(1)-C(11)-O(1)	-177.7(4)
C(19)-C(1)-C(11)-C(12)	56.8(5)
C(19)-C(1)-C(2)-C(9)	-64.8(5)
C(19)-C(1)-C(2)-C(3)	62.5(5)
C(16)-C(15)-C(14)-C(13)	0.7(8)
C(11B)-C(12B)-C(13B)-C(14B)	179.6(5)
C(11B)-C(12B)-C(17B)-C(16B)	180.0(5)
C(5)-C(6)-C(7)-C(8)	0.0(7)
C(3B)-C(8B)-C(7B)-C(6B)	0.3(7)
C(3B)-C(2B)-C(1B)-C(18B)	-172.3(4)
C(3B)-C(2B)-C(1B)-C(19B)	69.9(5)
C(3B)-C(2B)-C(1B)-C(11B)	-51.7(5)
C(3B)-C(2B)-C(9B)-C(10B)	130.2(5)
C(3B)-C(4B)-C(5B)-C(6B)	-0.3(7)
C(9B)-C(2B)-C(1B)-C(18B)	60.0(5)
C(9B)-C(2B)-C(1B)-C(19B)	-57.8(5)
C(9B)-C(2B)-C(1B)-C(11B)	-179.4(4)
C(9B)-C(2B)-C(3B)-C(8B)	49.2(6)
C(9B)-C(2B)-C(3B)-C(4B)	-127.9(4)
C(7)-C(6)-C(5)-C(4)	0.4(7)
C(7)-C(8)-C(3)-C(2)	-177.7(4)
C(7)-C(8)-C(3)-C(4)	0.0(7)
C(13B)-C(12B)-C(11B)-O(1B)	-36.2(6)
C(13B)-C(12B)-C(11B)-C(1B)	85.7(5)
C(13B)-C(12B)-C(17B)-C(16B)	-0.9(7)
C(13B)-C(14B)-C(15B)-C(16B)	0.2(8)
C(14B)-C(15B)-C(16B)-C(17B)	-0.7(8)
C(10)-C(9)-C(2)-C(1)	-120.1(5)
C(10)-C(9)-C(2)-C(3)	110.7(5)
C(17B)-C(12B)-C(11B)-O(1B)	142.9(4)
C(17B)-C(12B)-C(11B)-C(1B)	-95.2(5)
C(17B)-C(12B)-C(13B)-C(14B)	0.5(7)

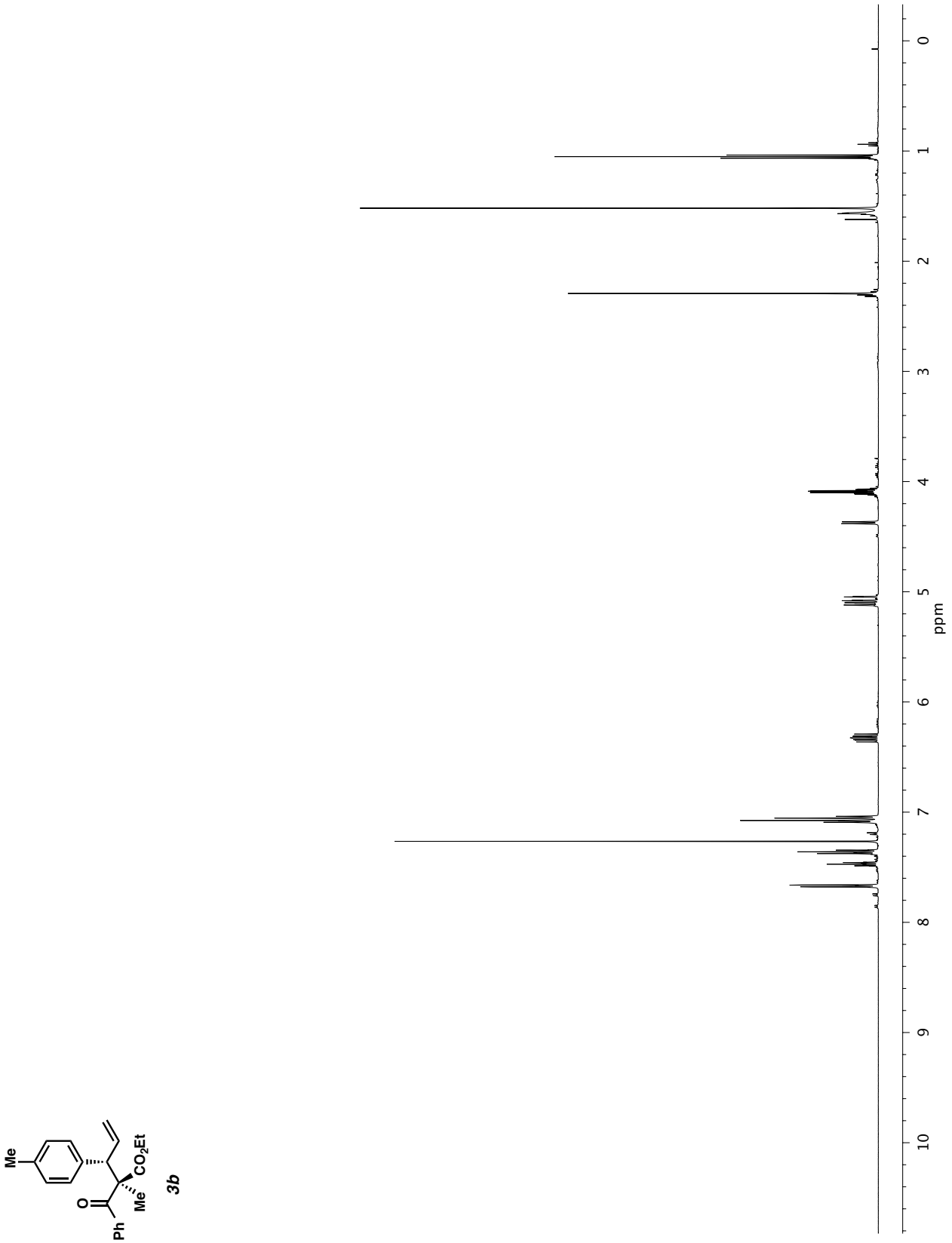
Symmetry transformations used to generate equivalent atoms:



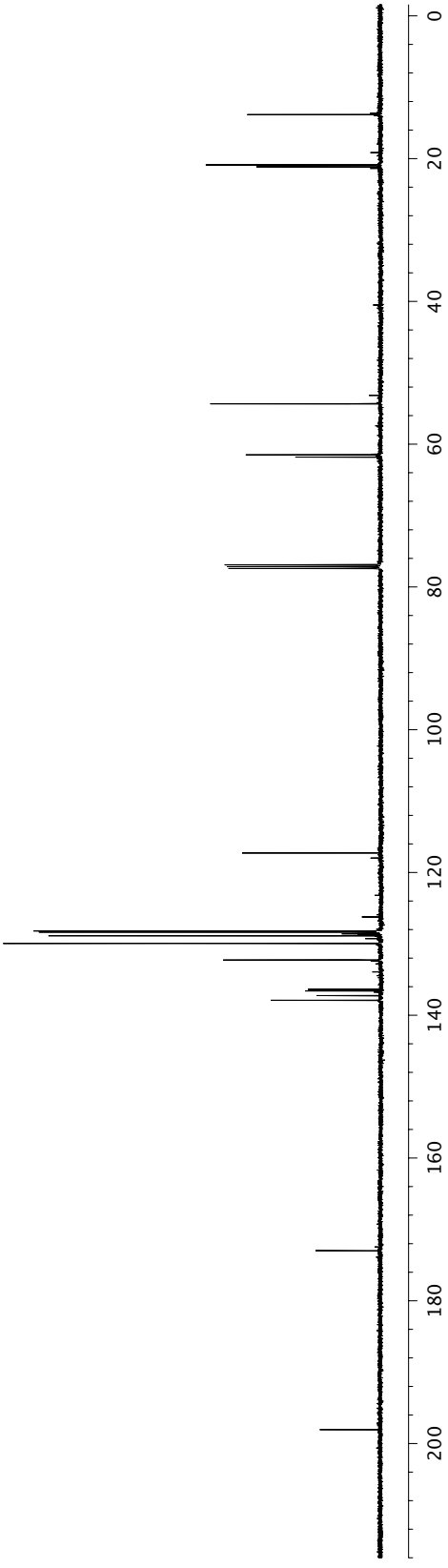
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**.



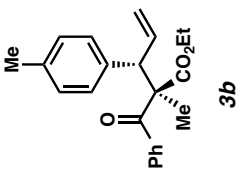
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3a**.



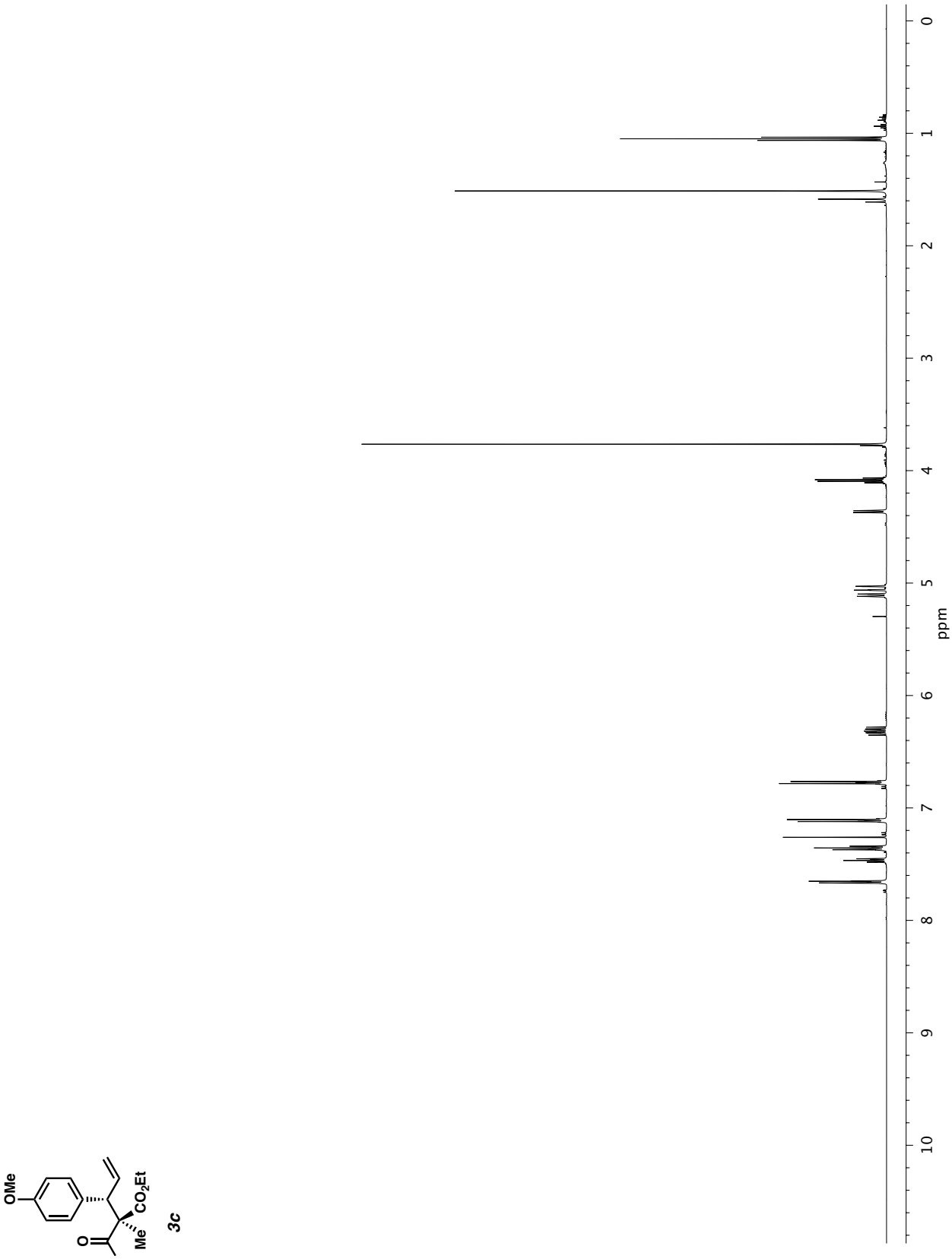
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**.



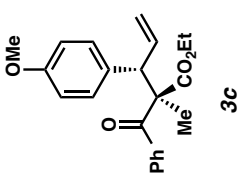
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3b**.



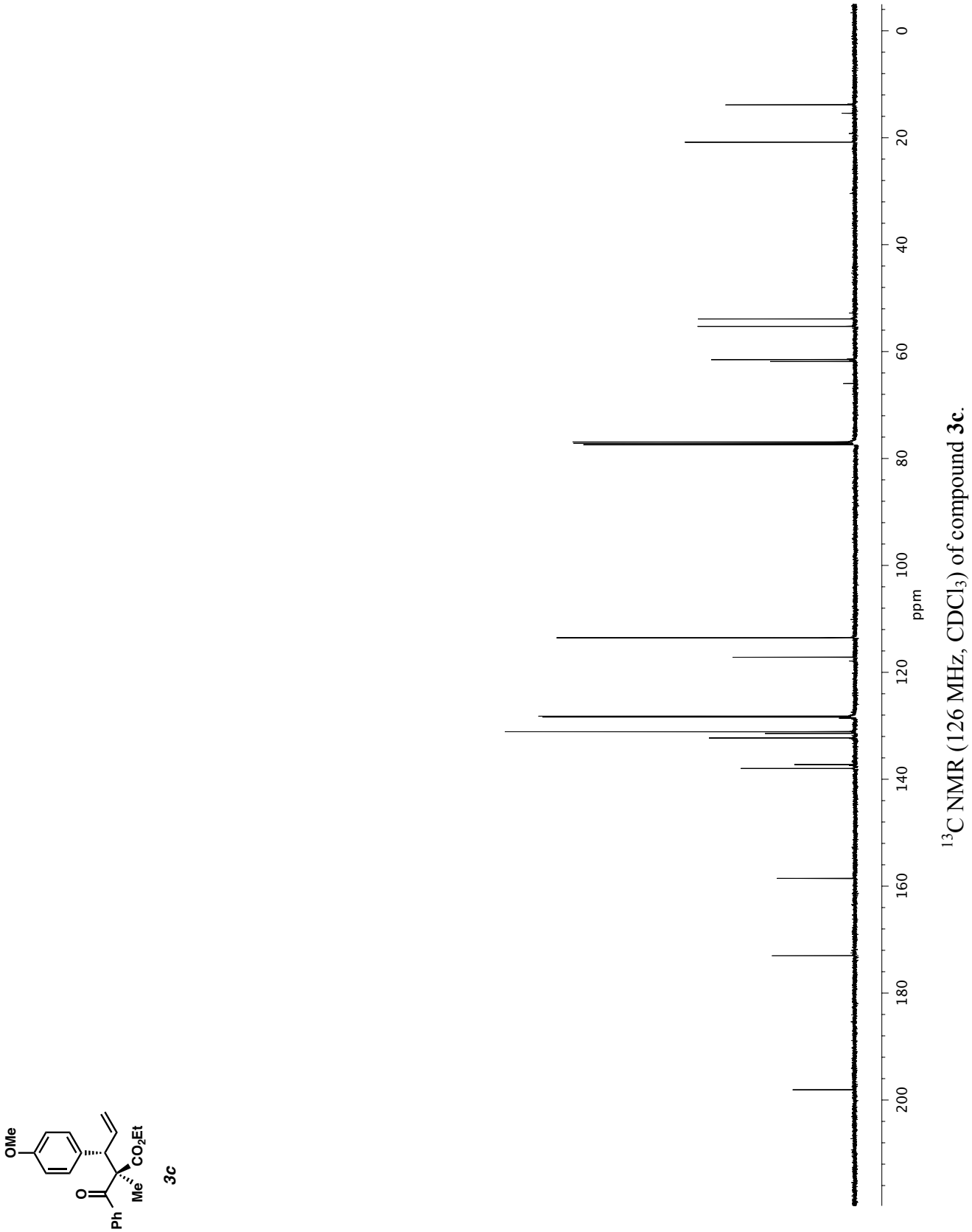
3b



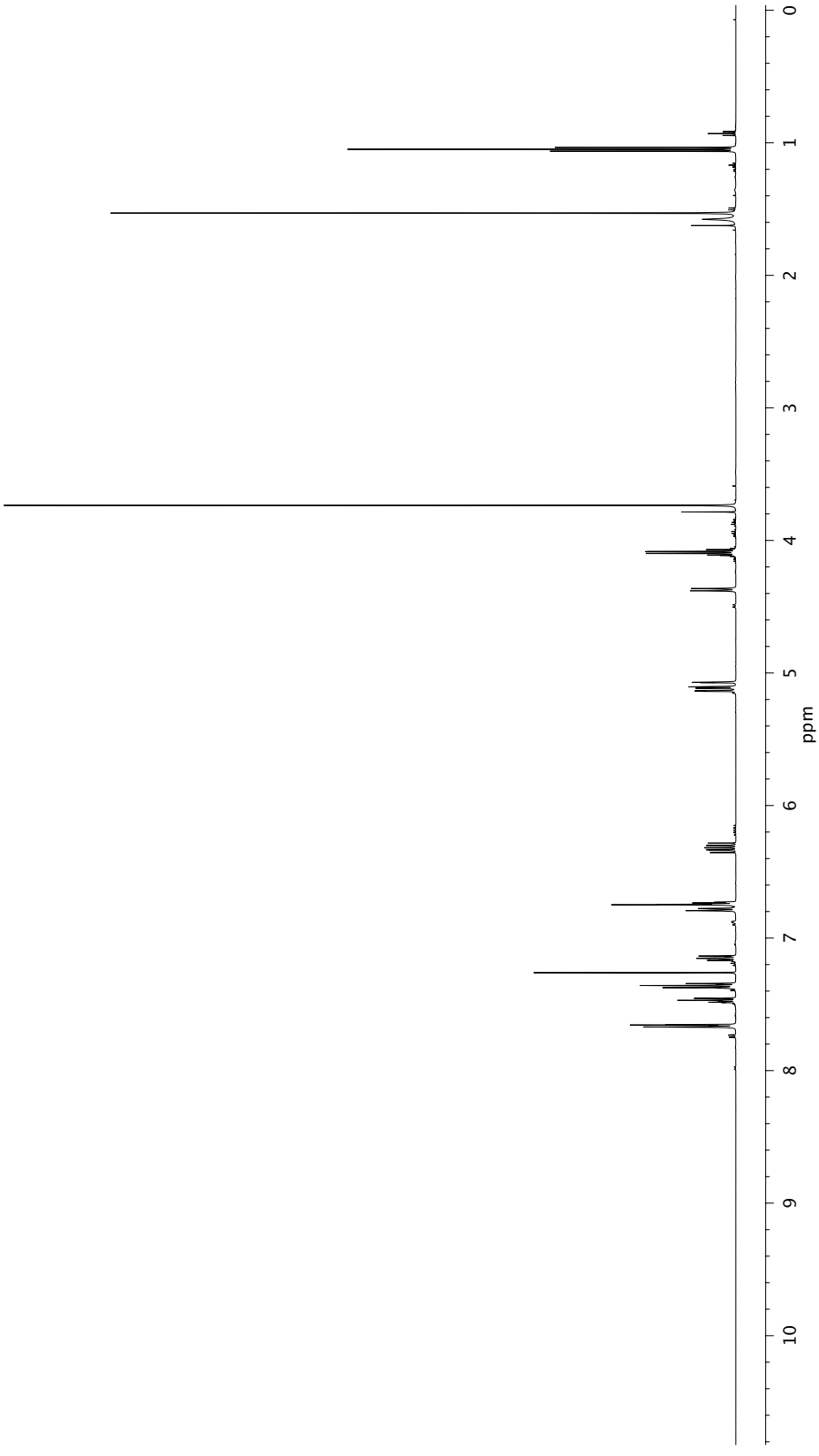
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**.



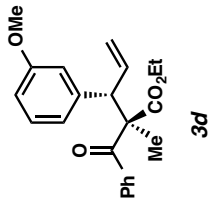
3c



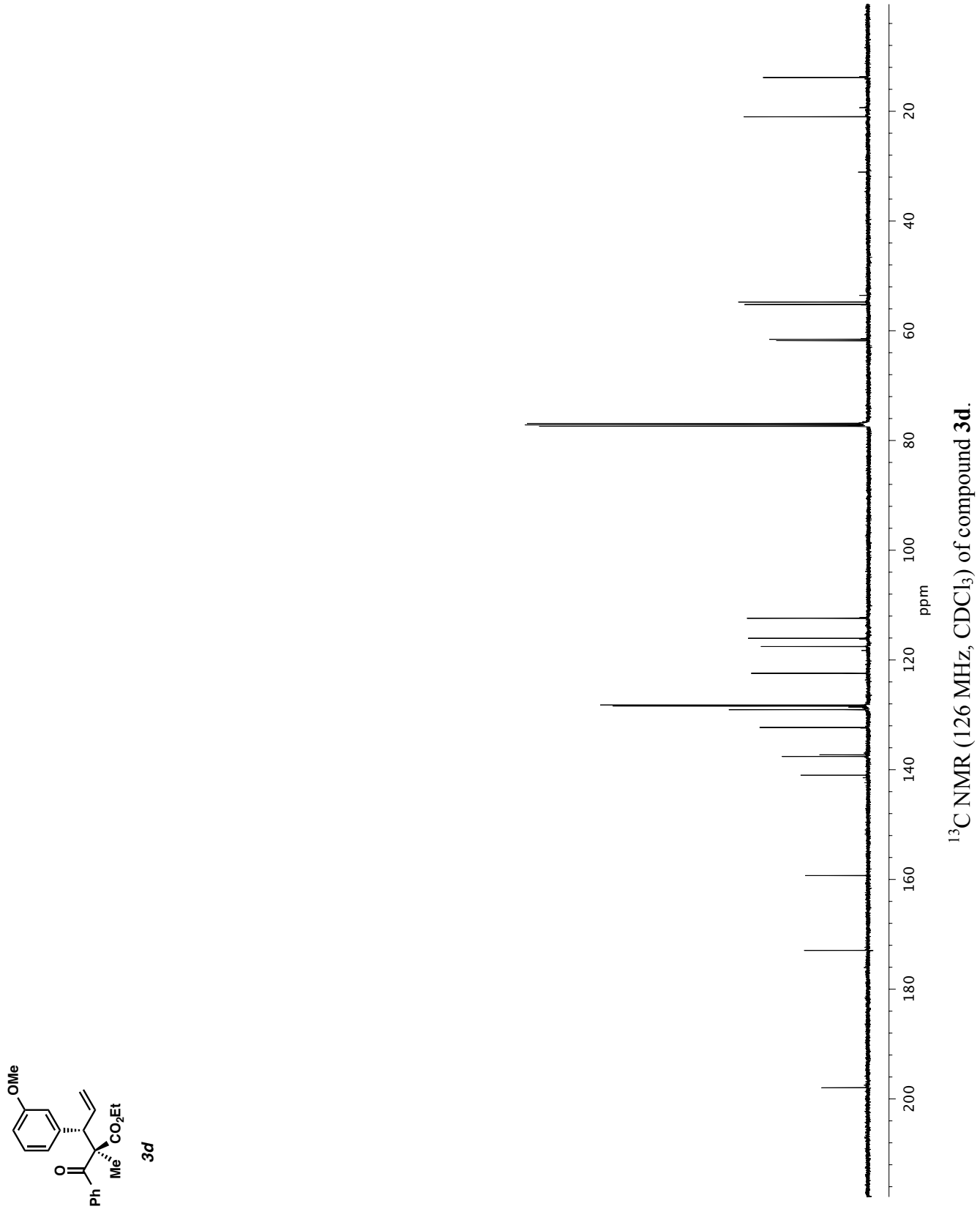
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3c**.



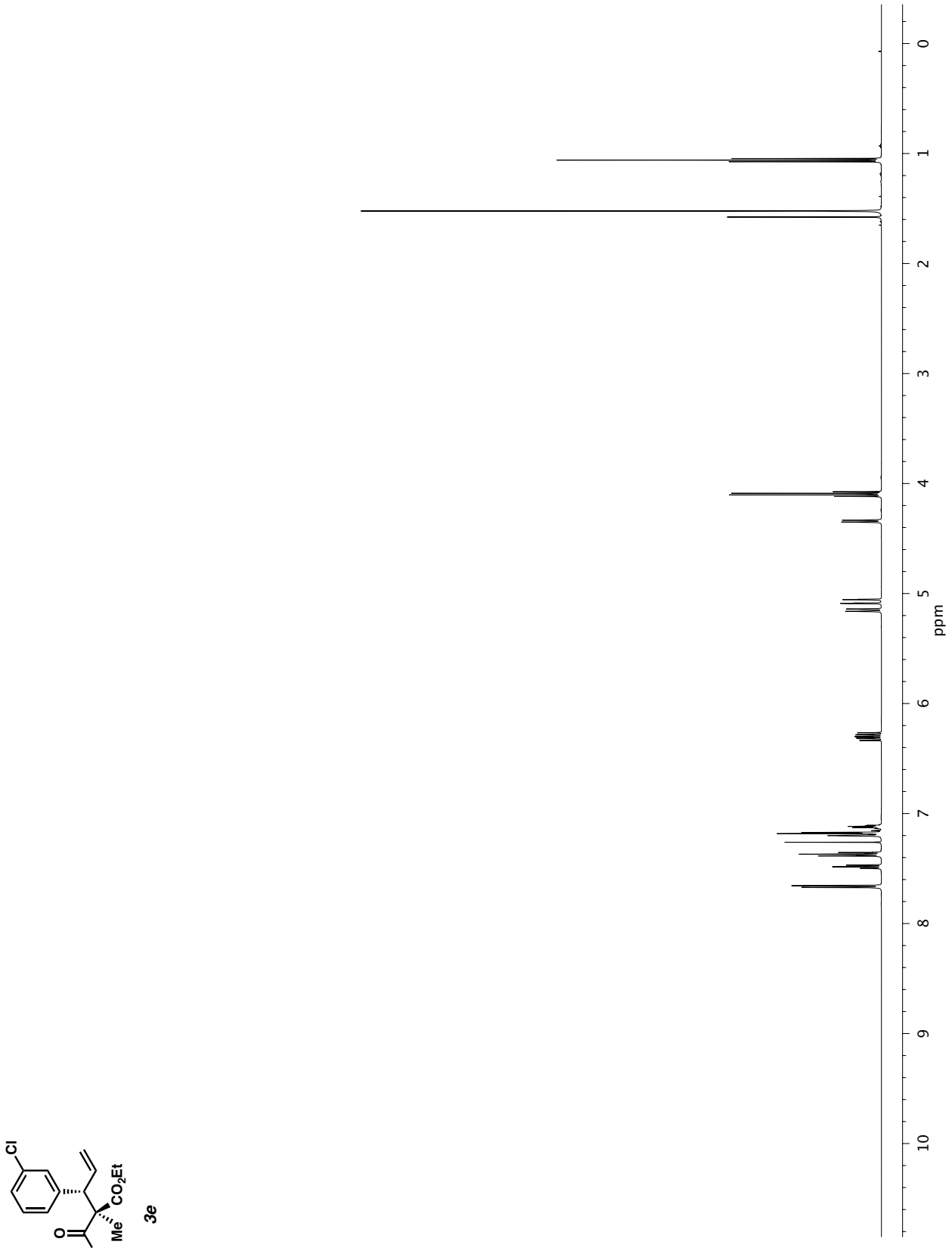
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**.



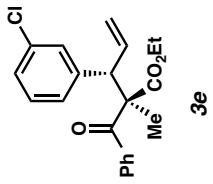
3d



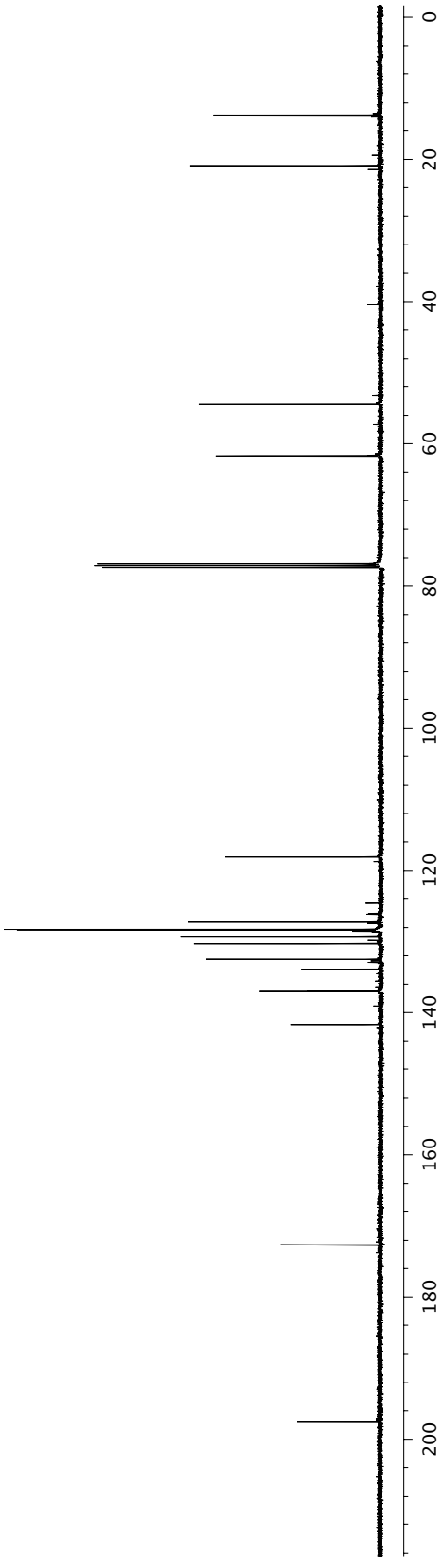
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**.



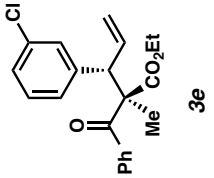
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**.



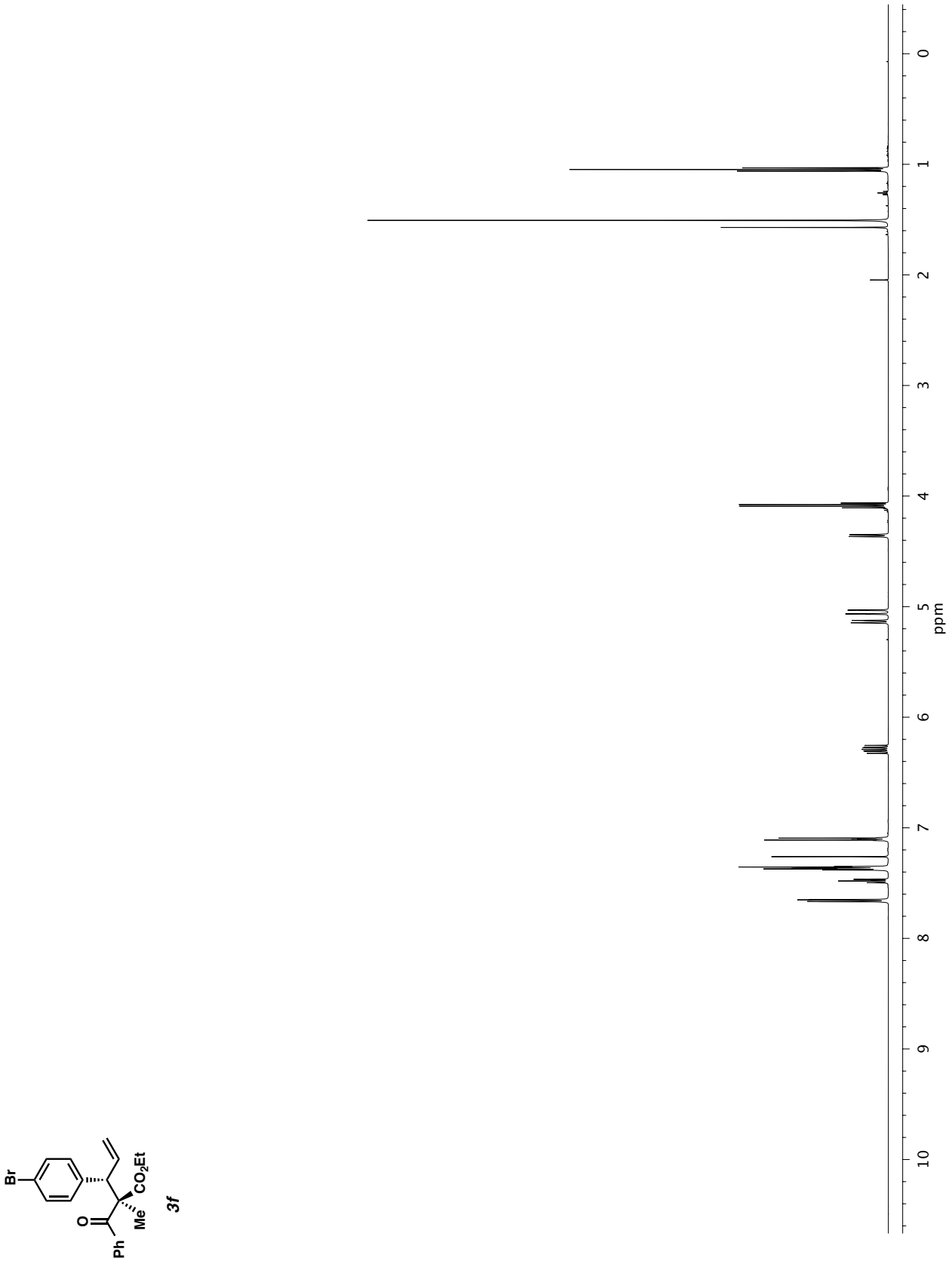
3e



^{13}C NMR (126 MHz, $CDCl_3$) of compound **3e**.

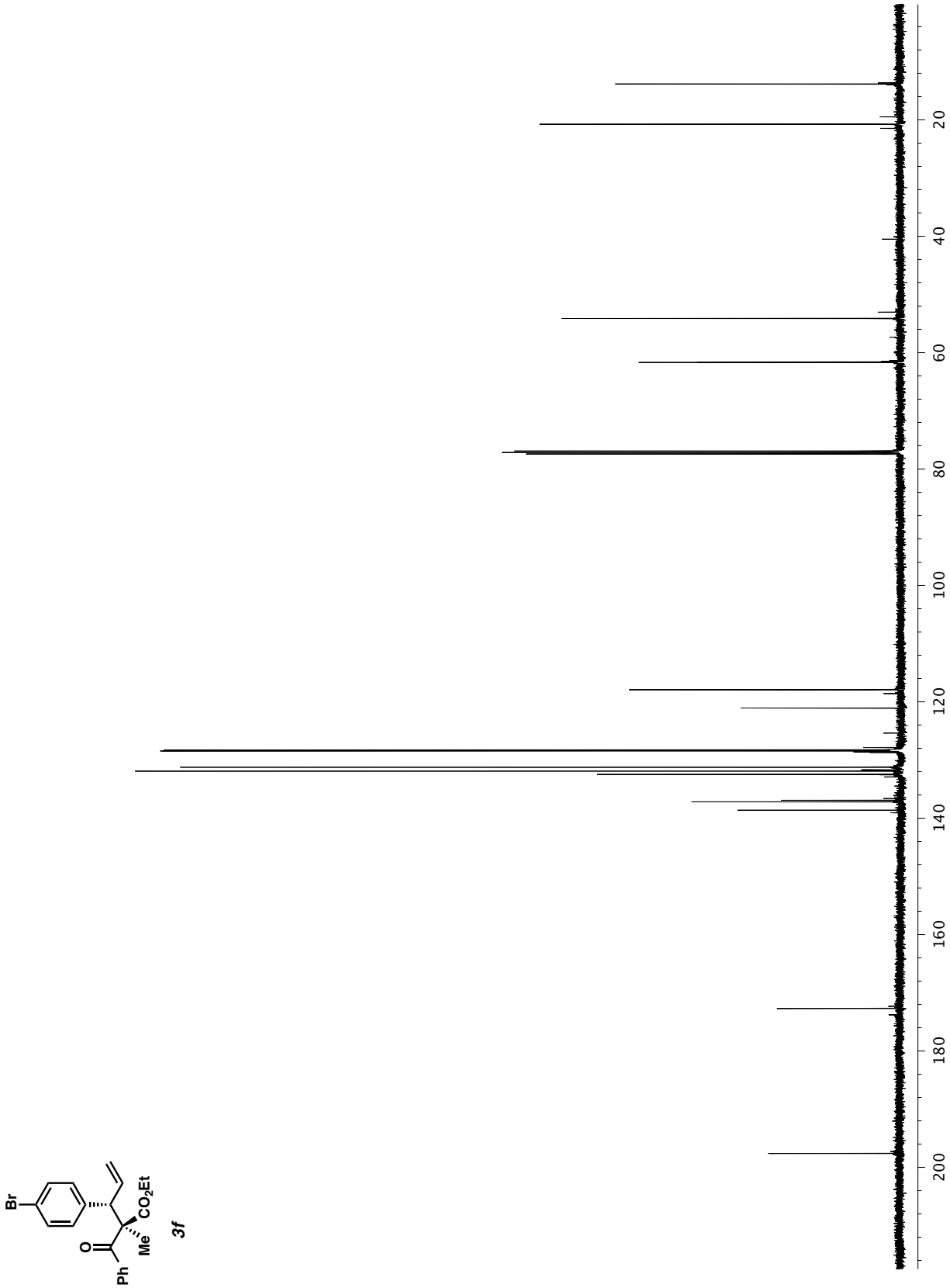


3e

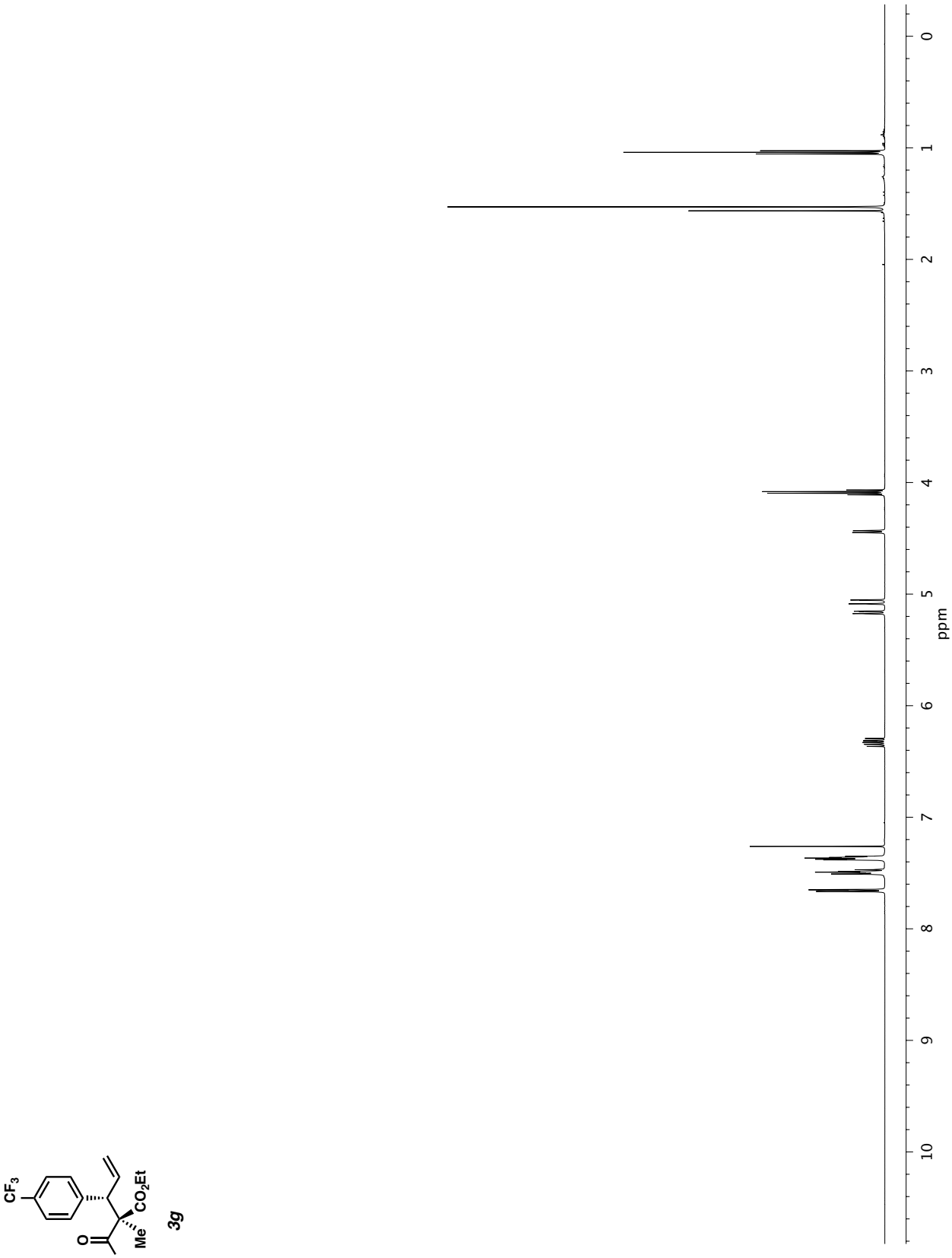


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**.

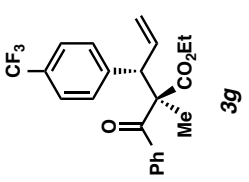
3f



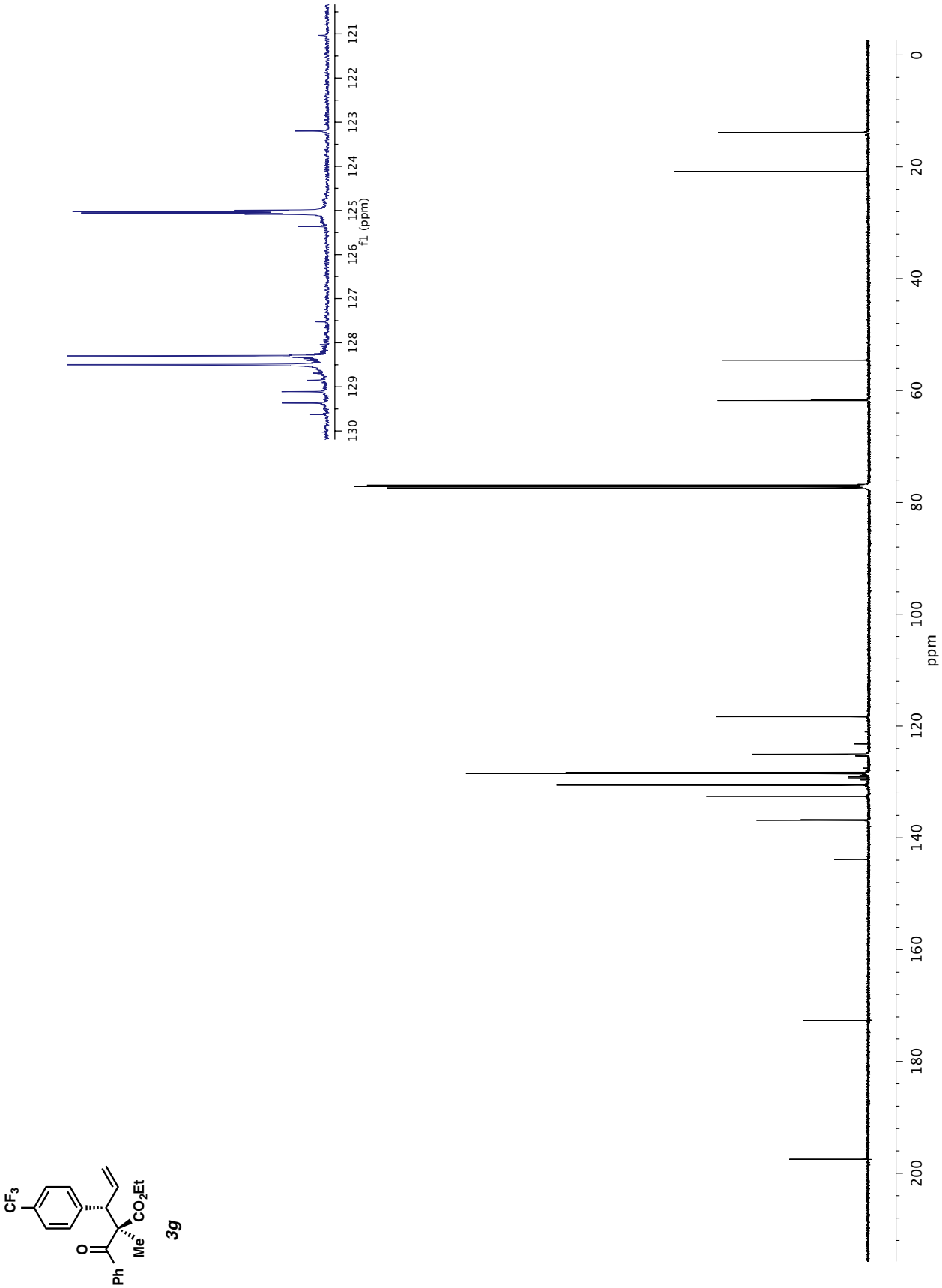
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**.



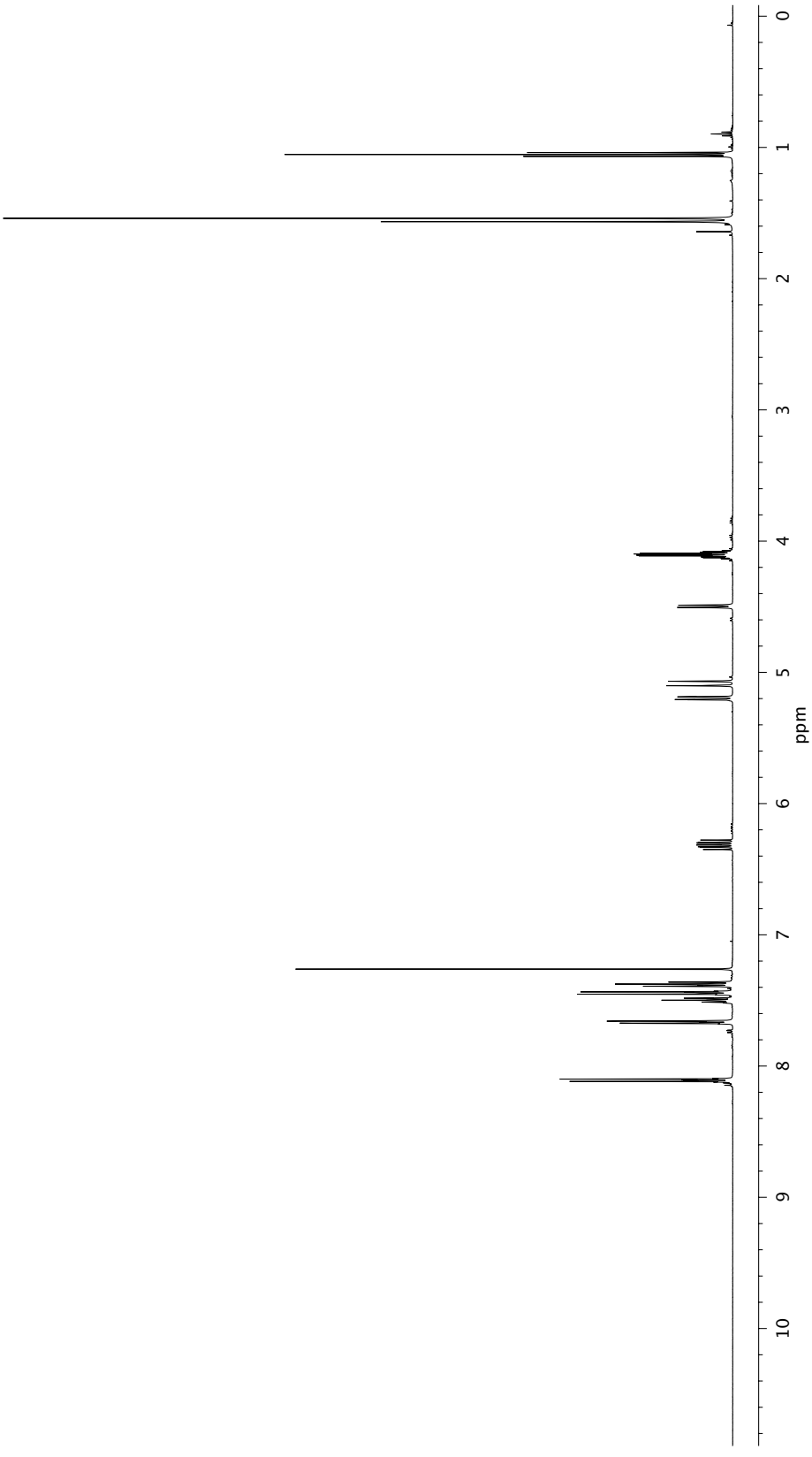
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**.



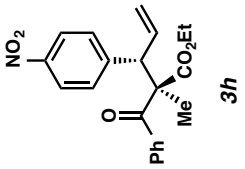
3g



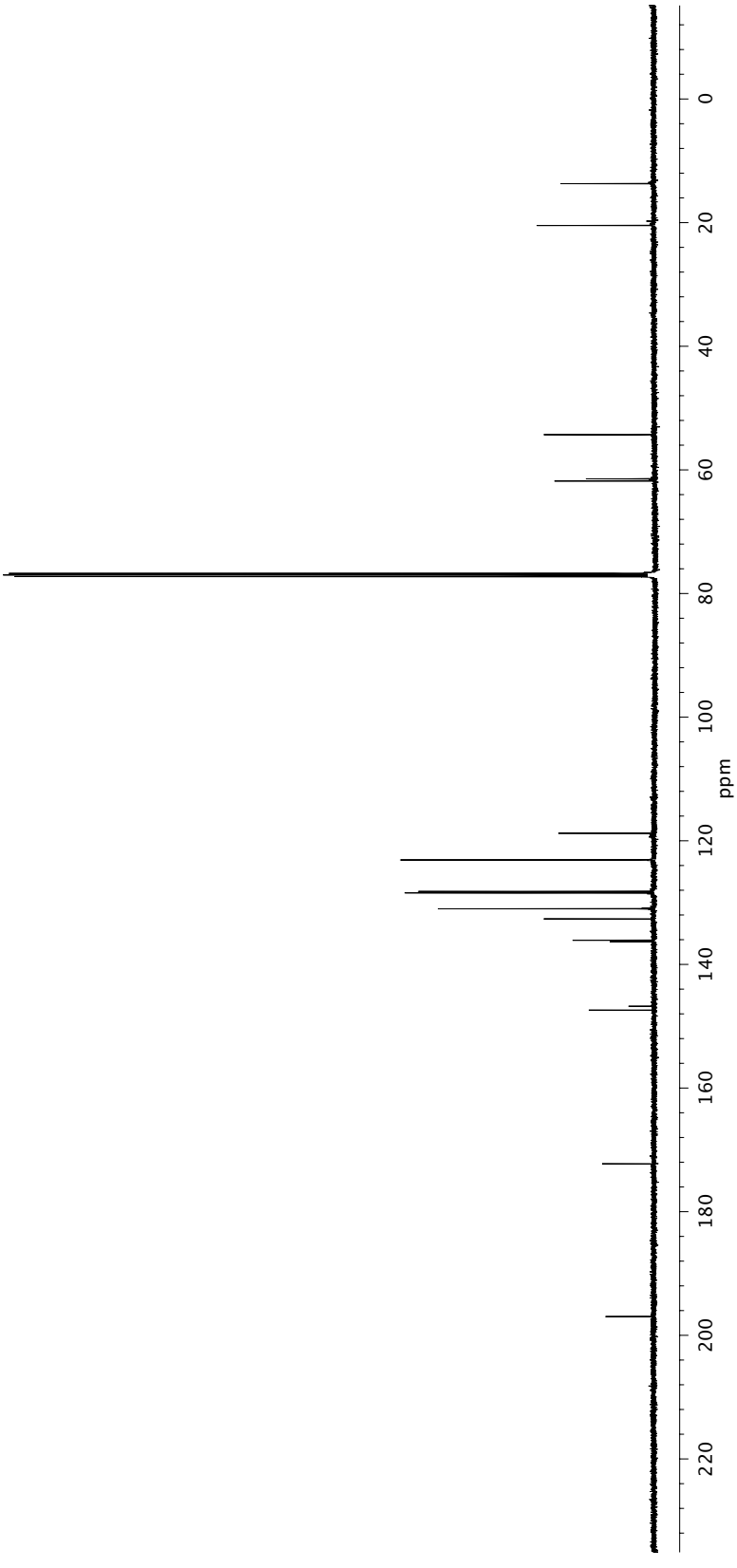
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3g**.



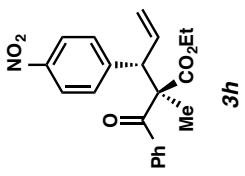
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3h**.



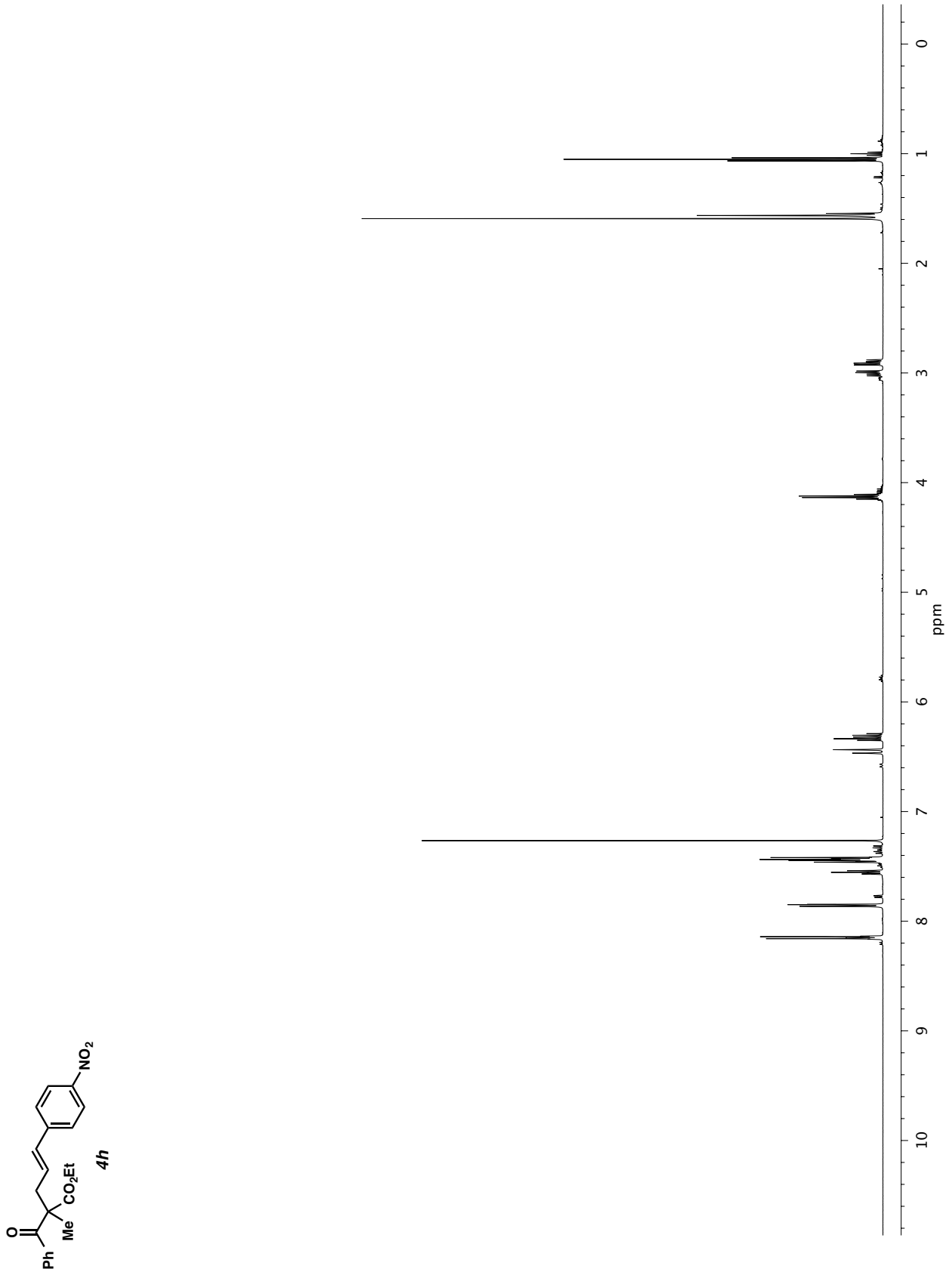
3h



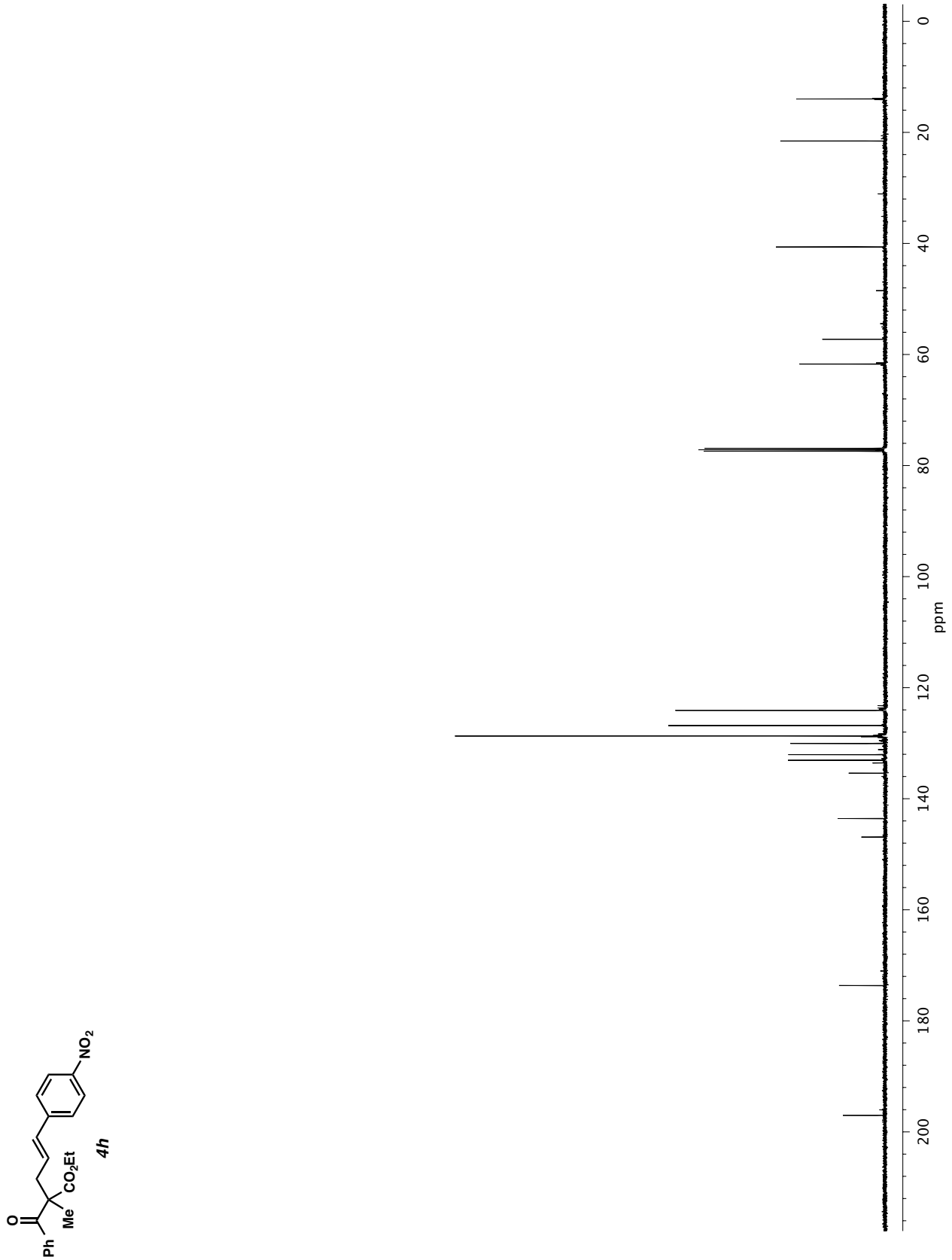
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3g**.



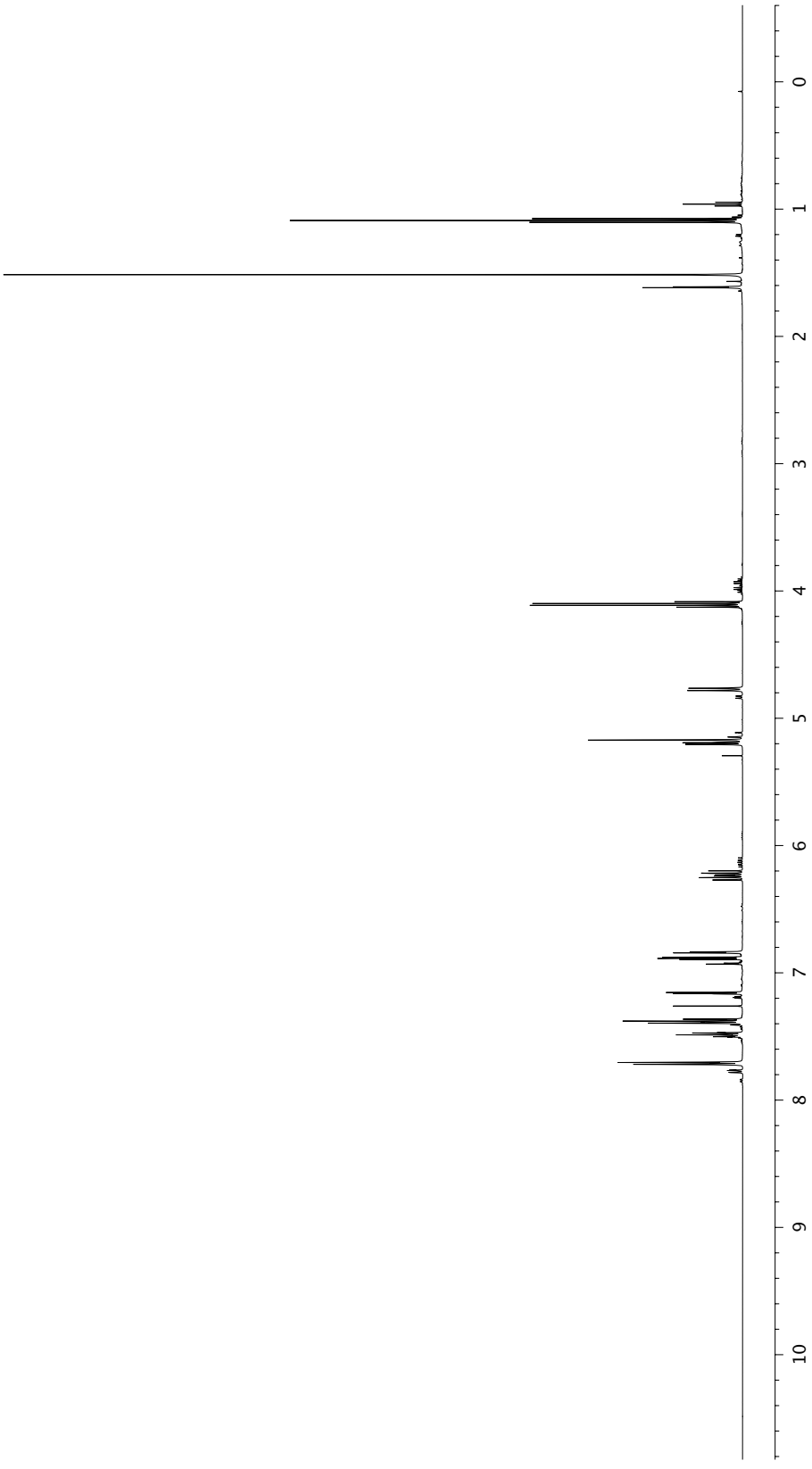
3h



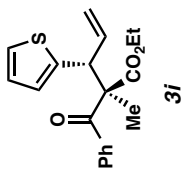
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h**.



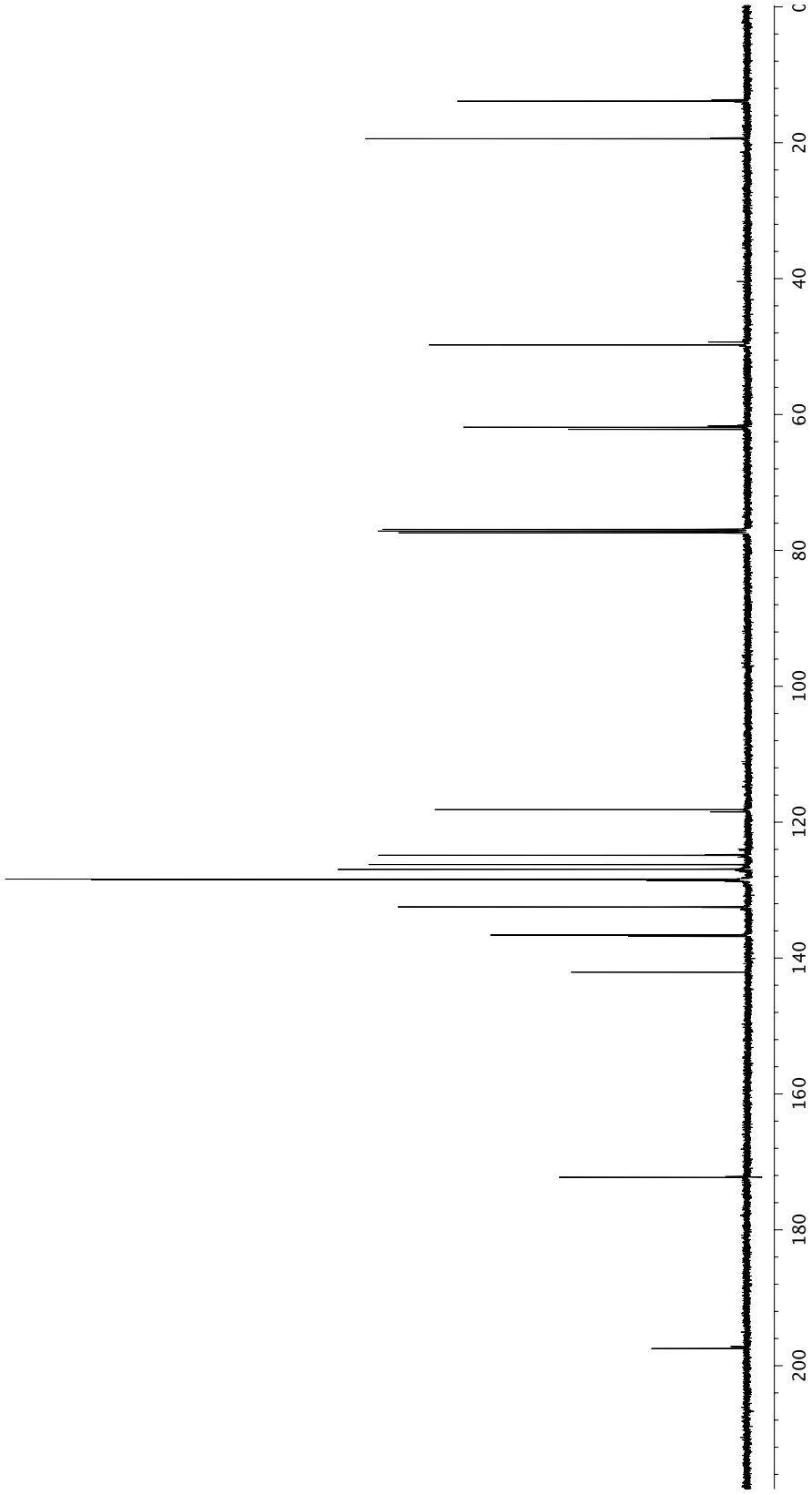
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4h**.



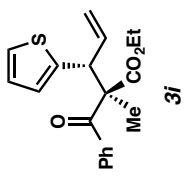
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i**.



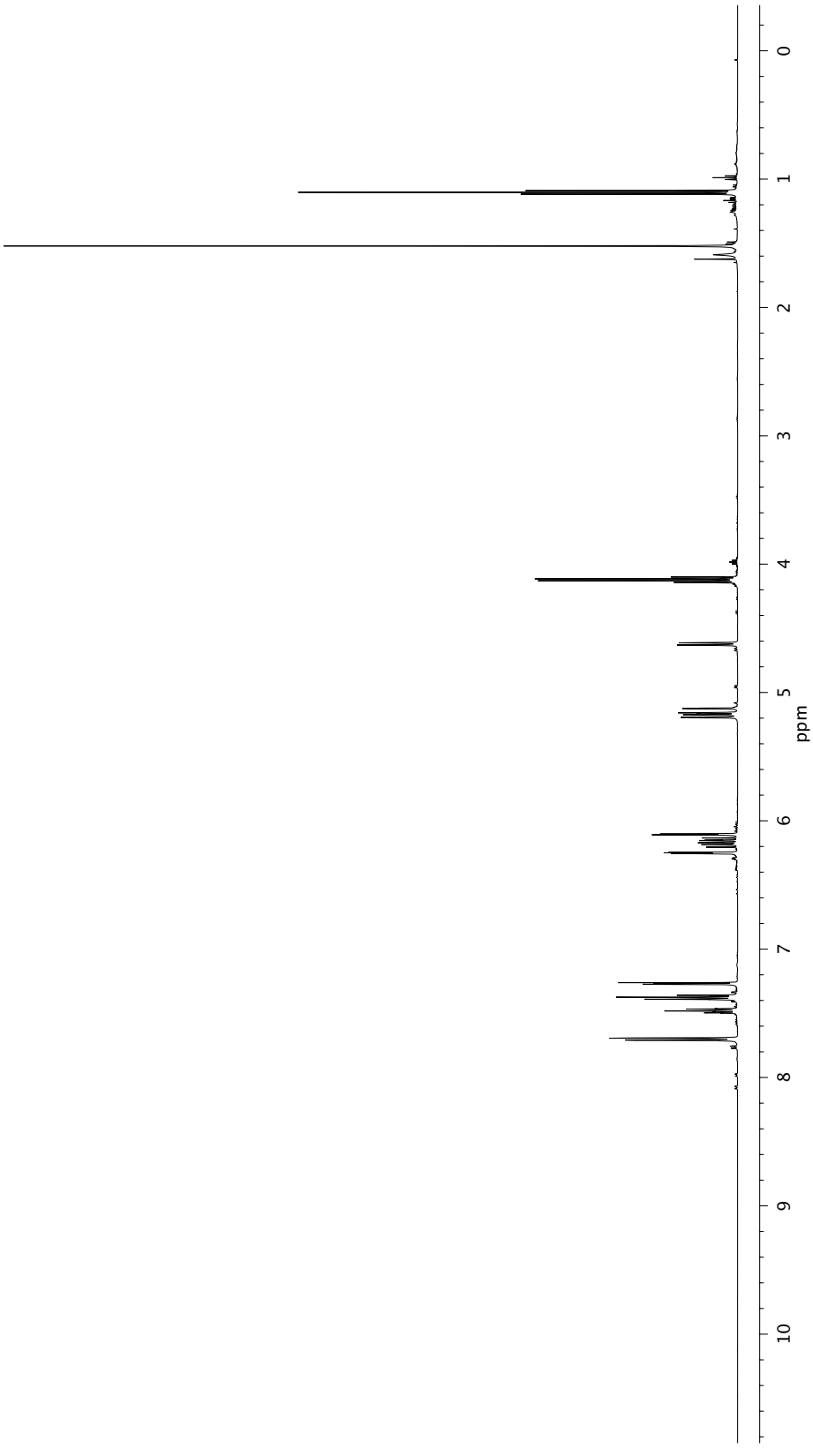
3i



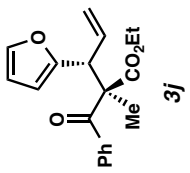
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3i**.



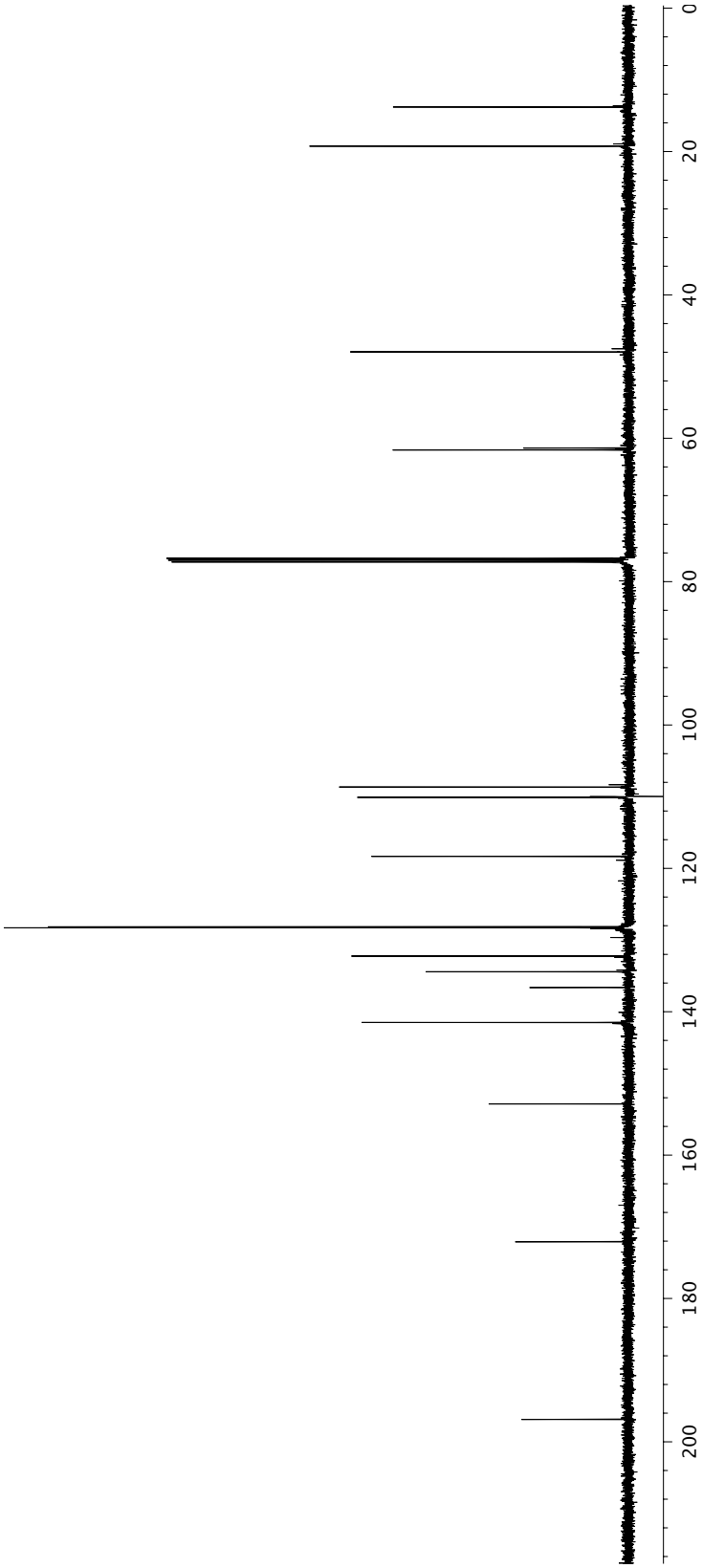
3i



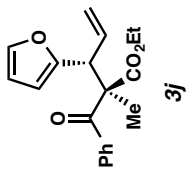
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3j**.



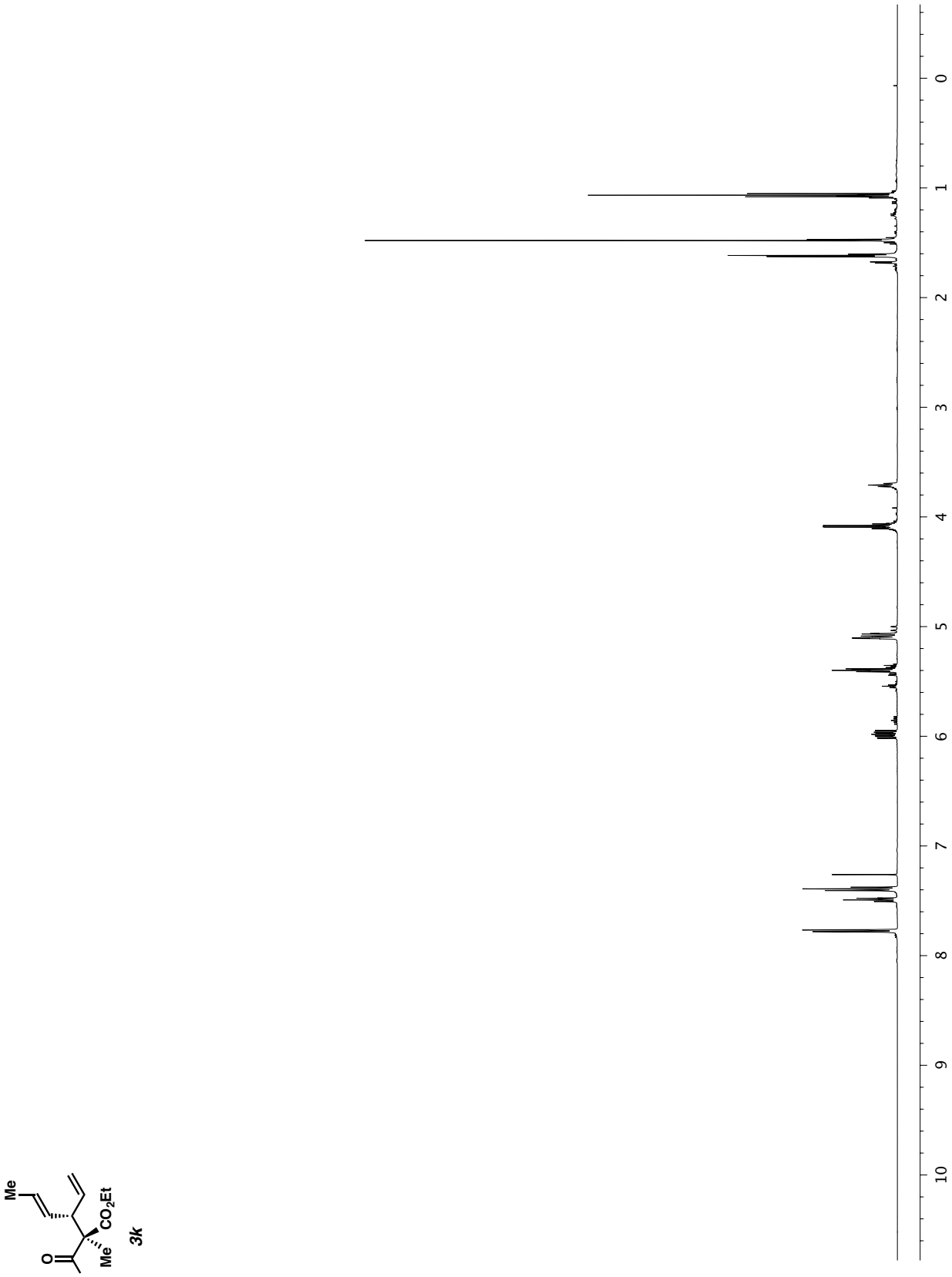
3j



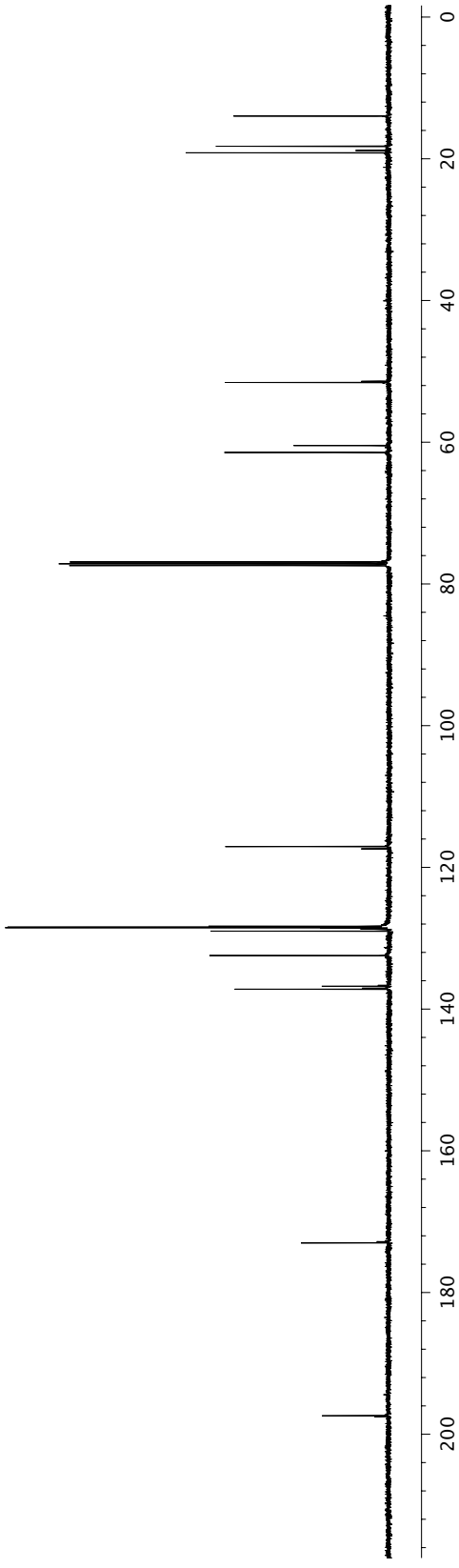
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3j**.



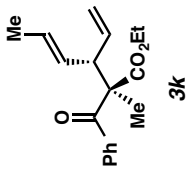
3j

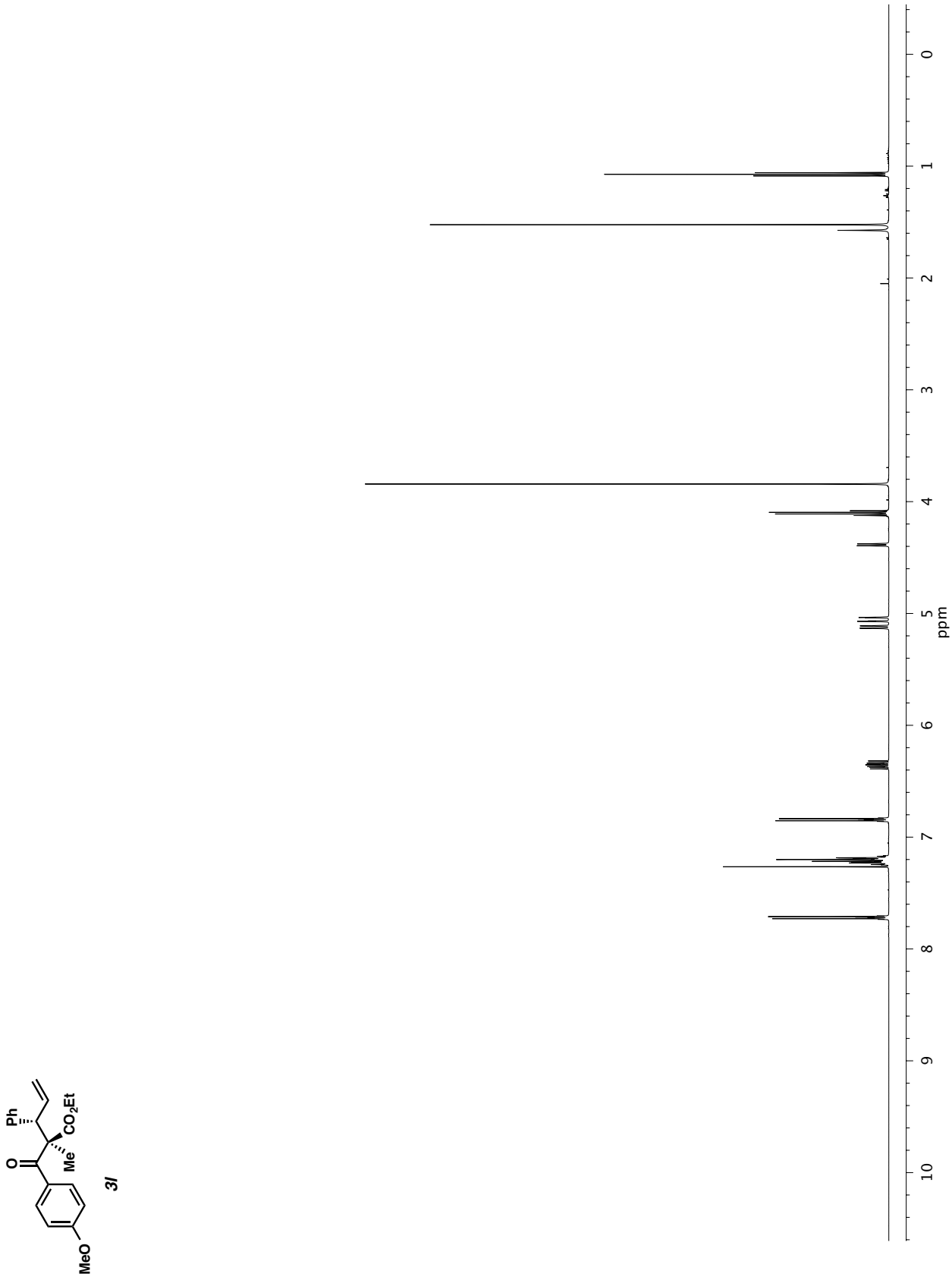


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**.

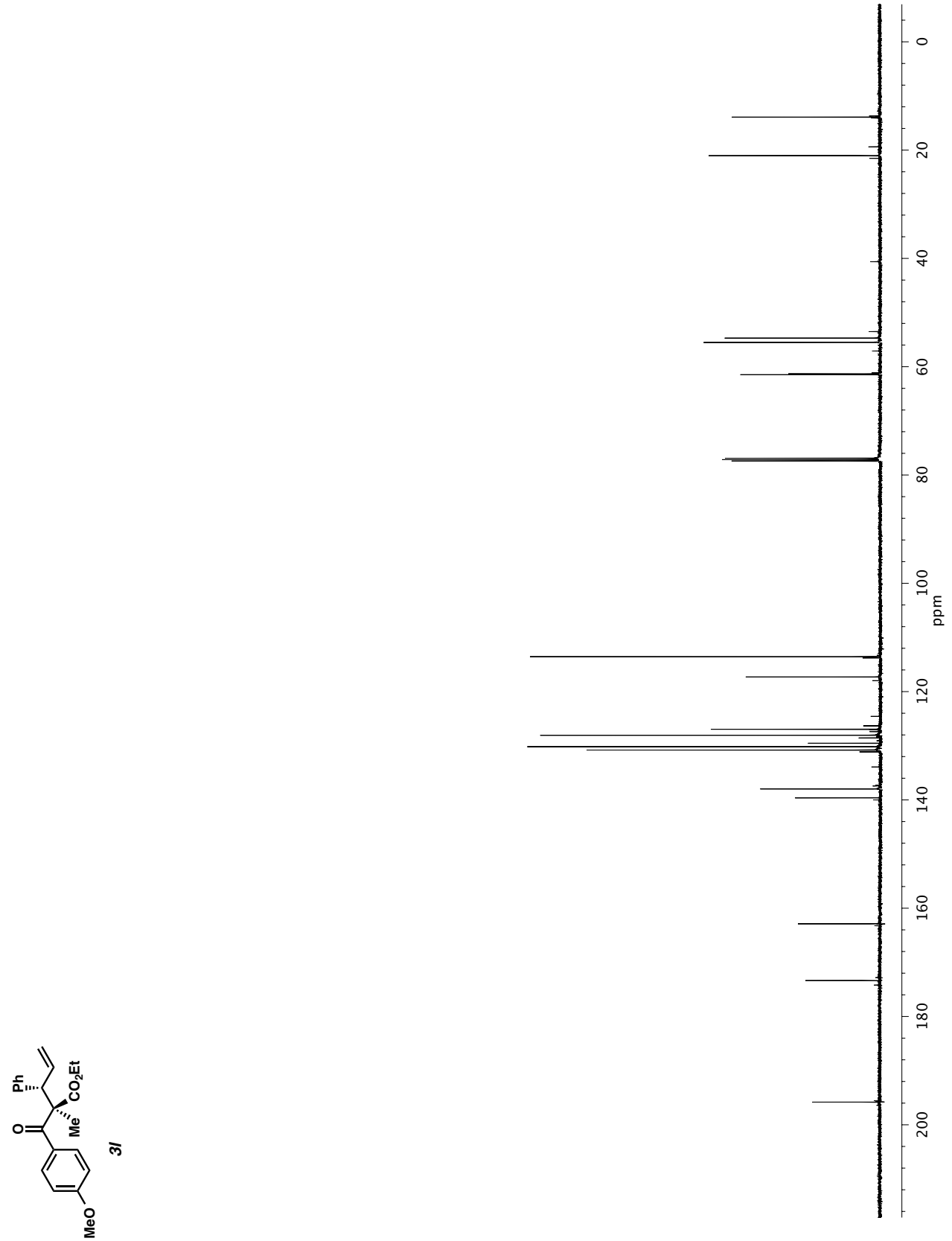


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3k**.

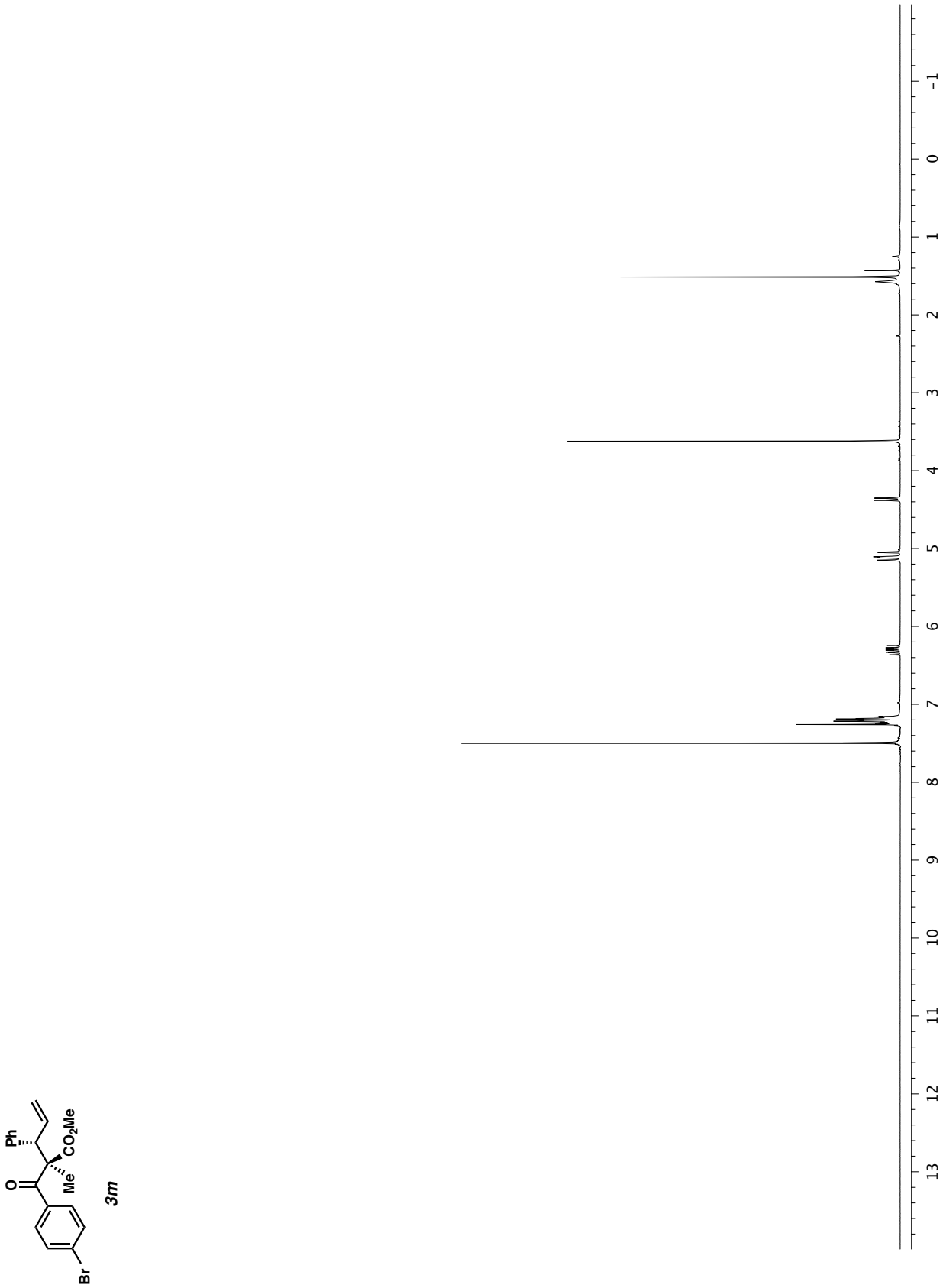




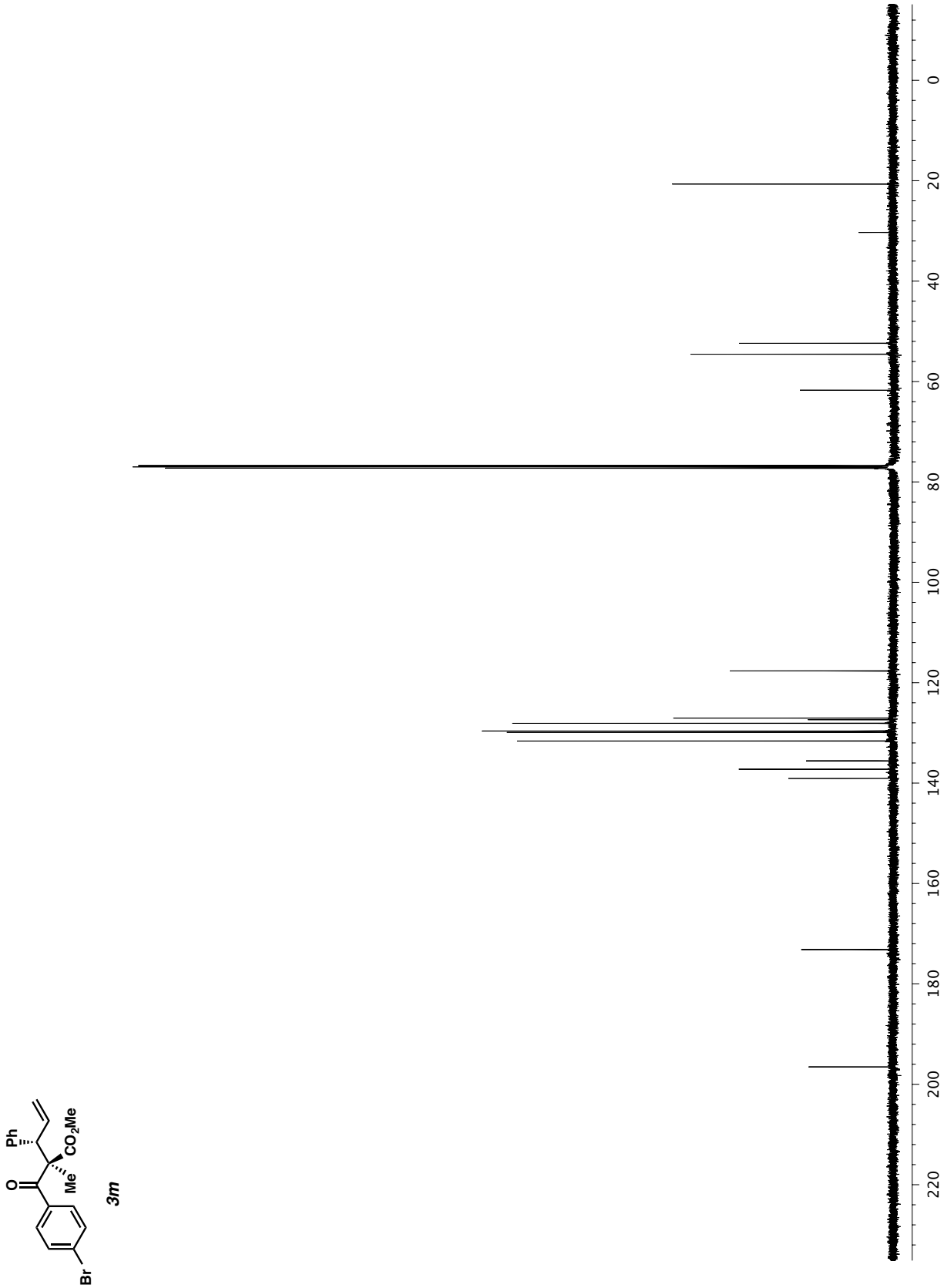
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**.



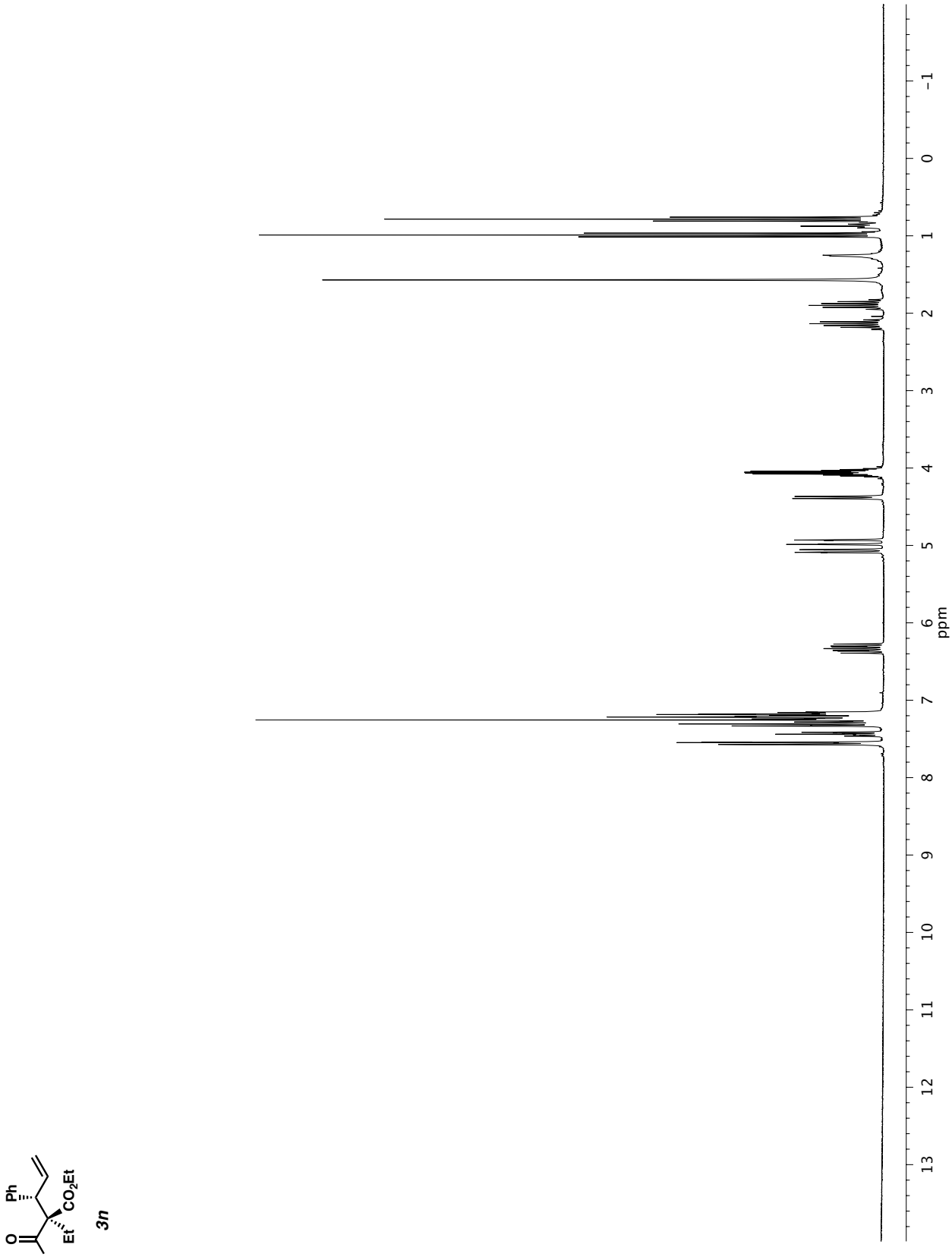
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3l**.



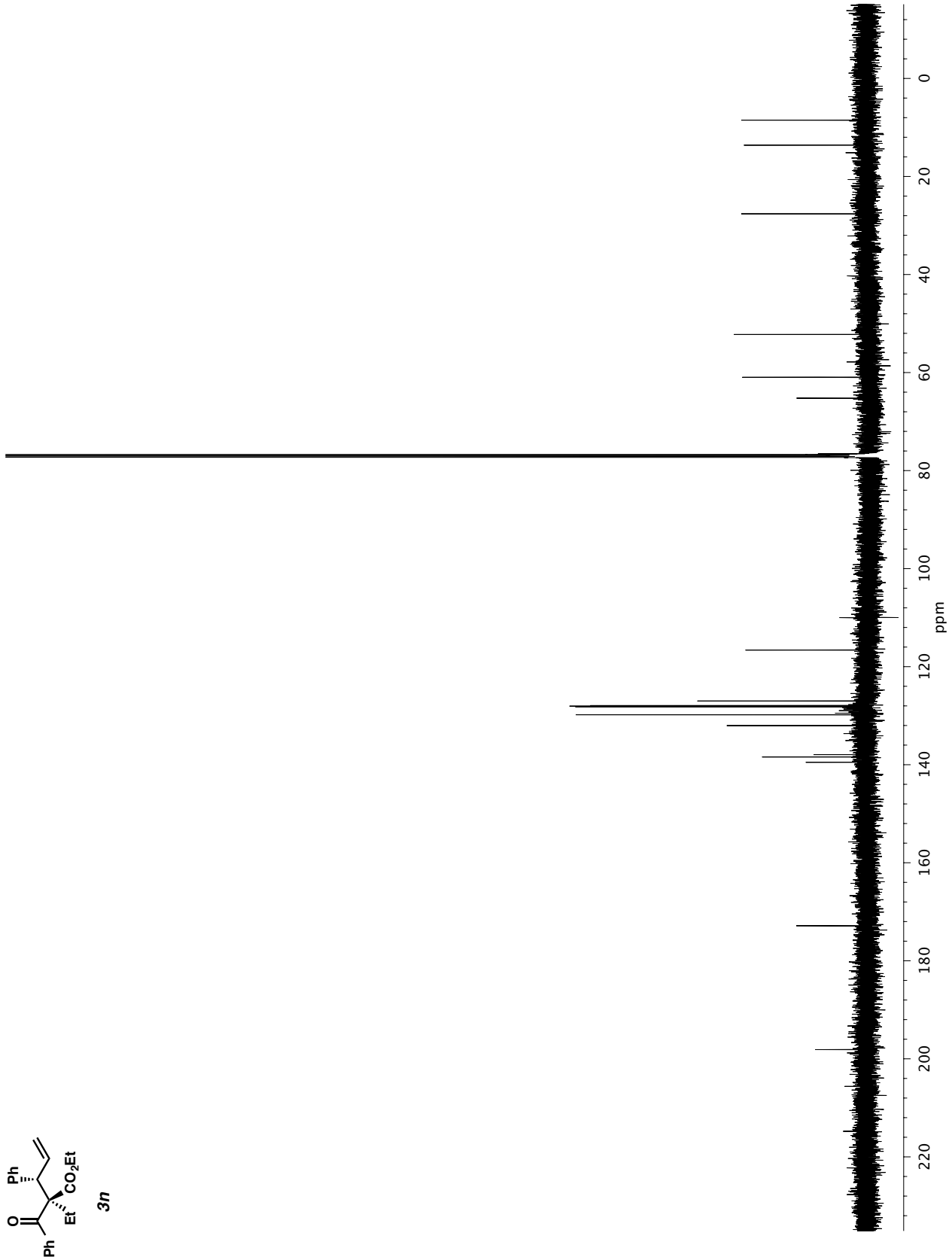
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**.



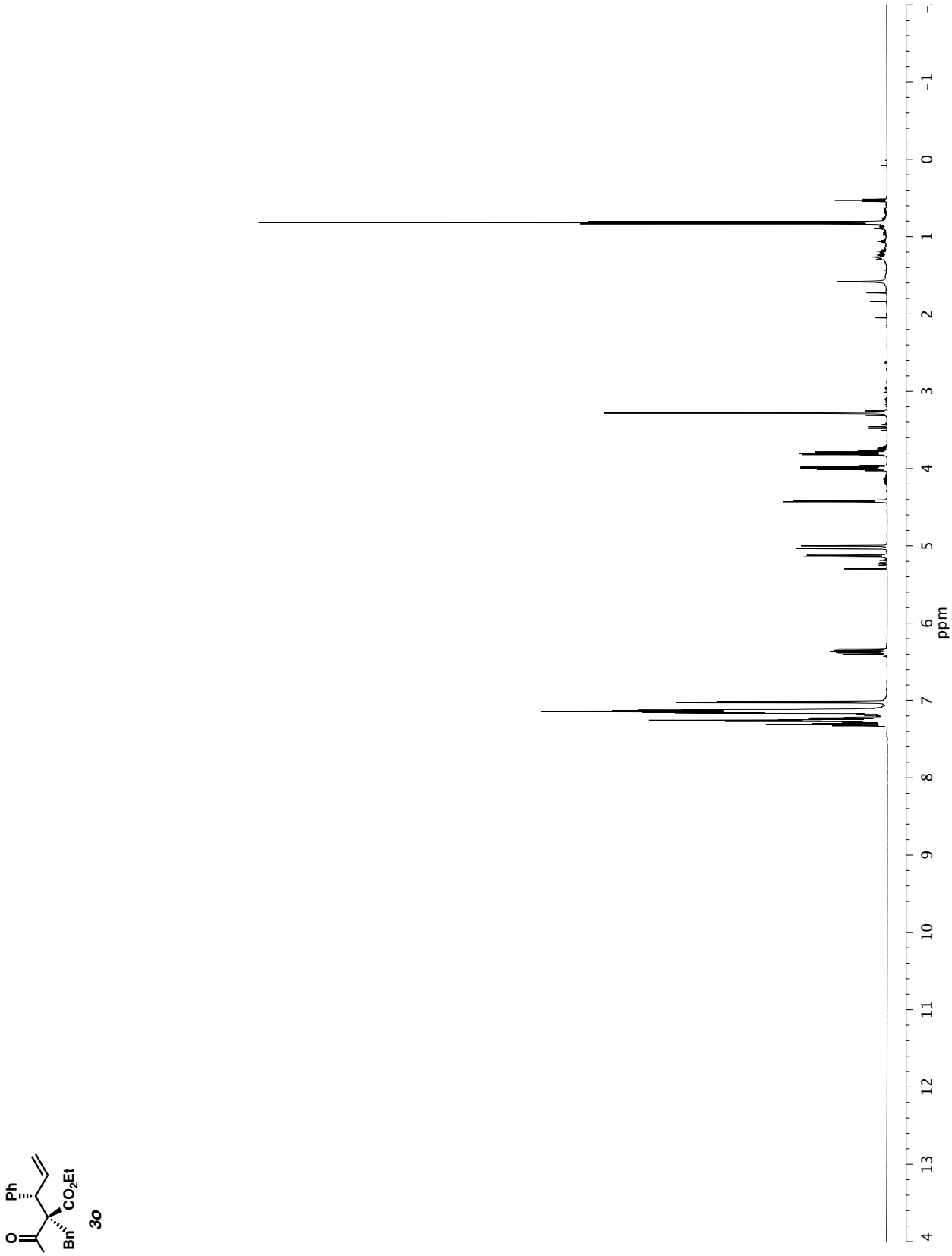
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3m**.



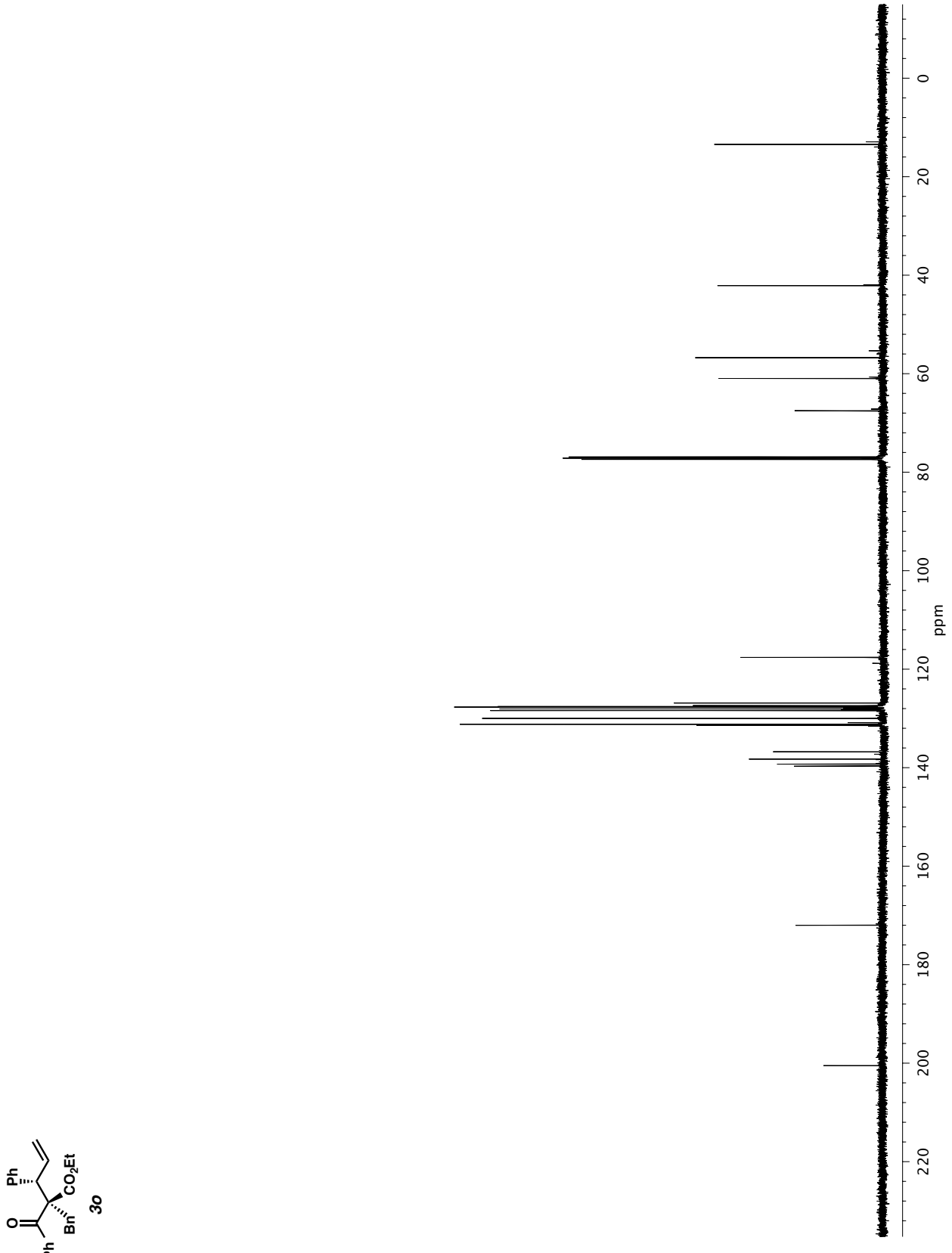
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3n**.



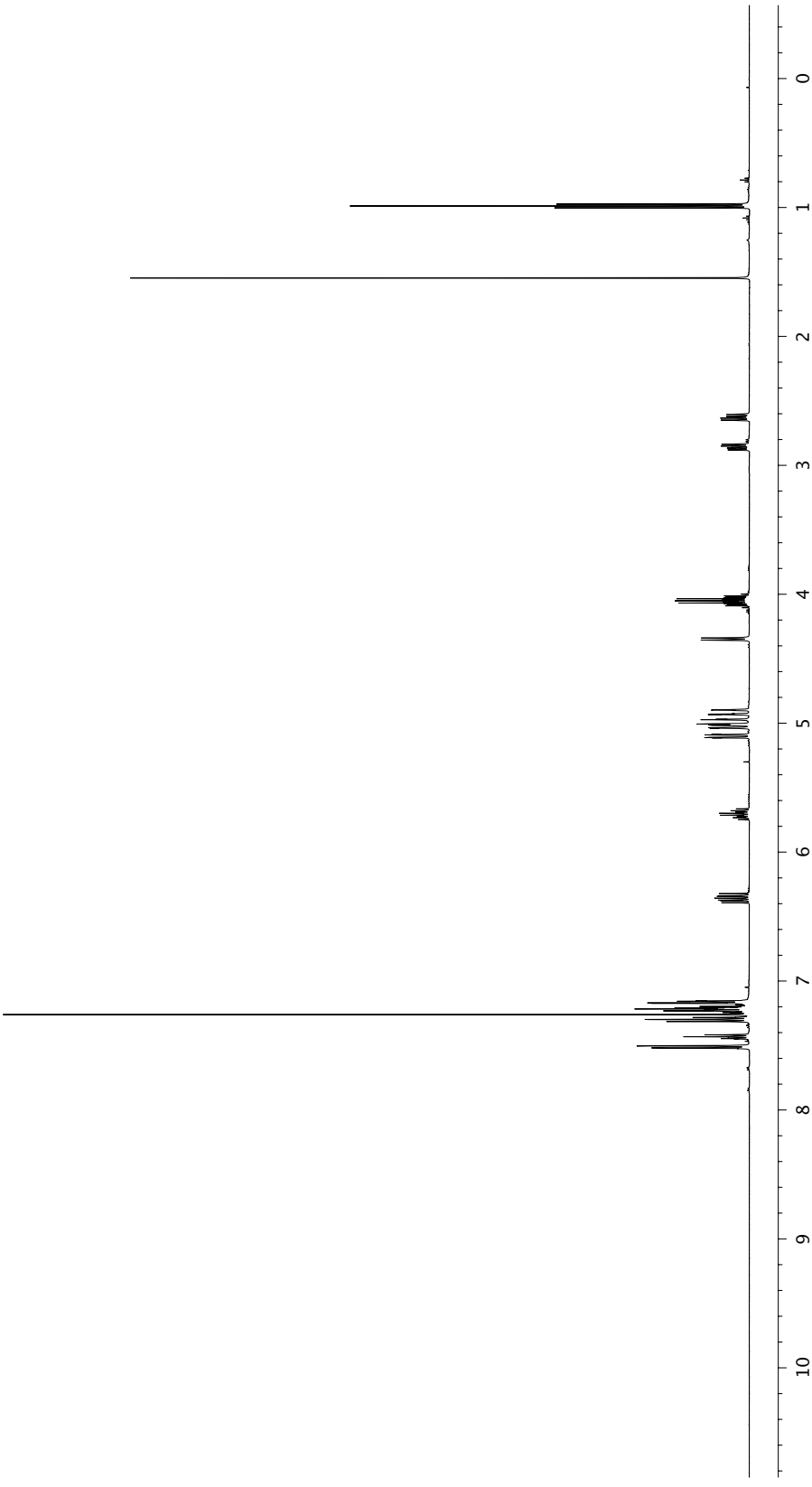
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3n**.



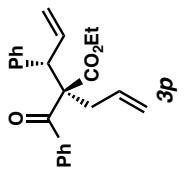
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o**.

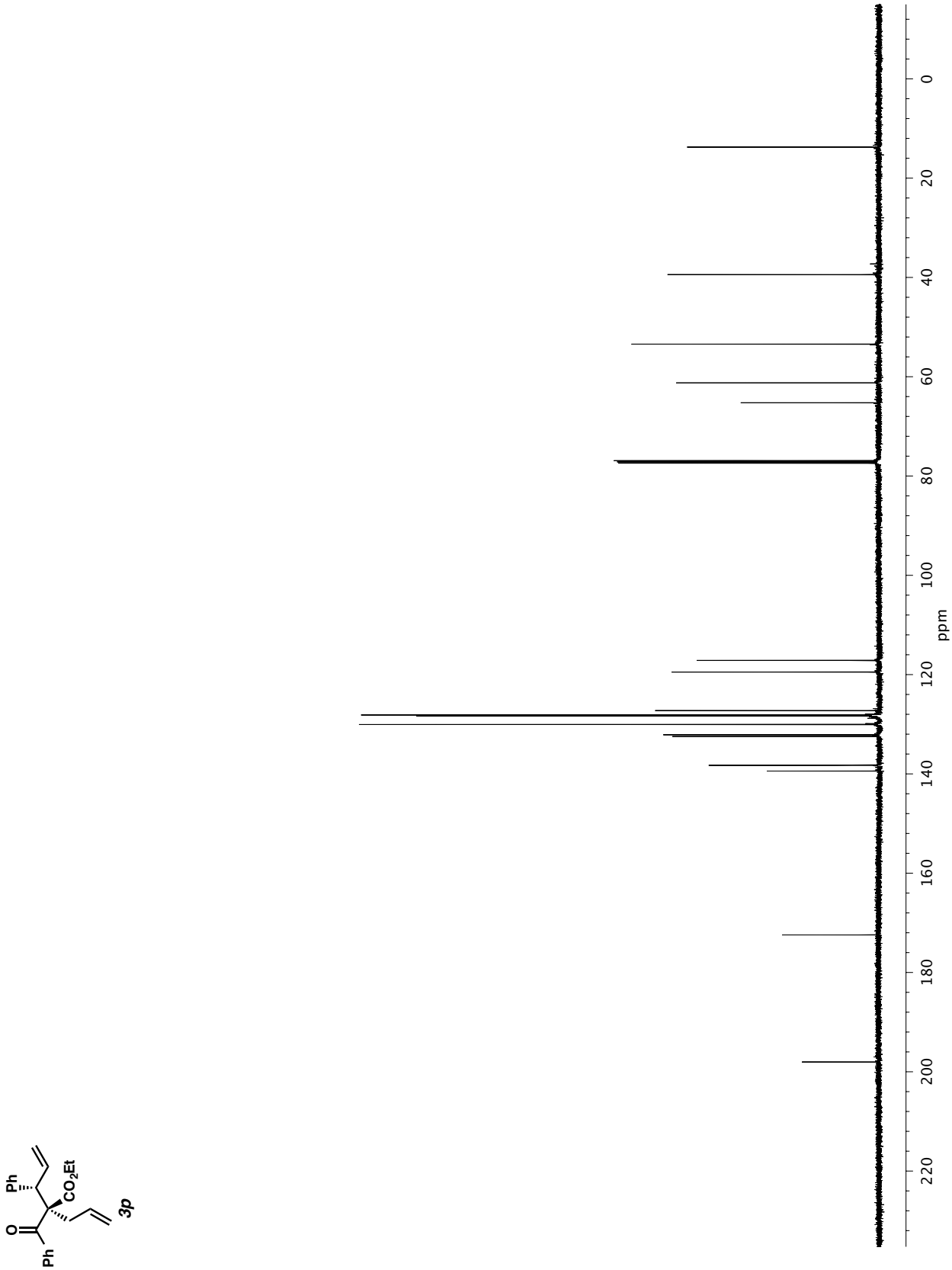


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3o**.

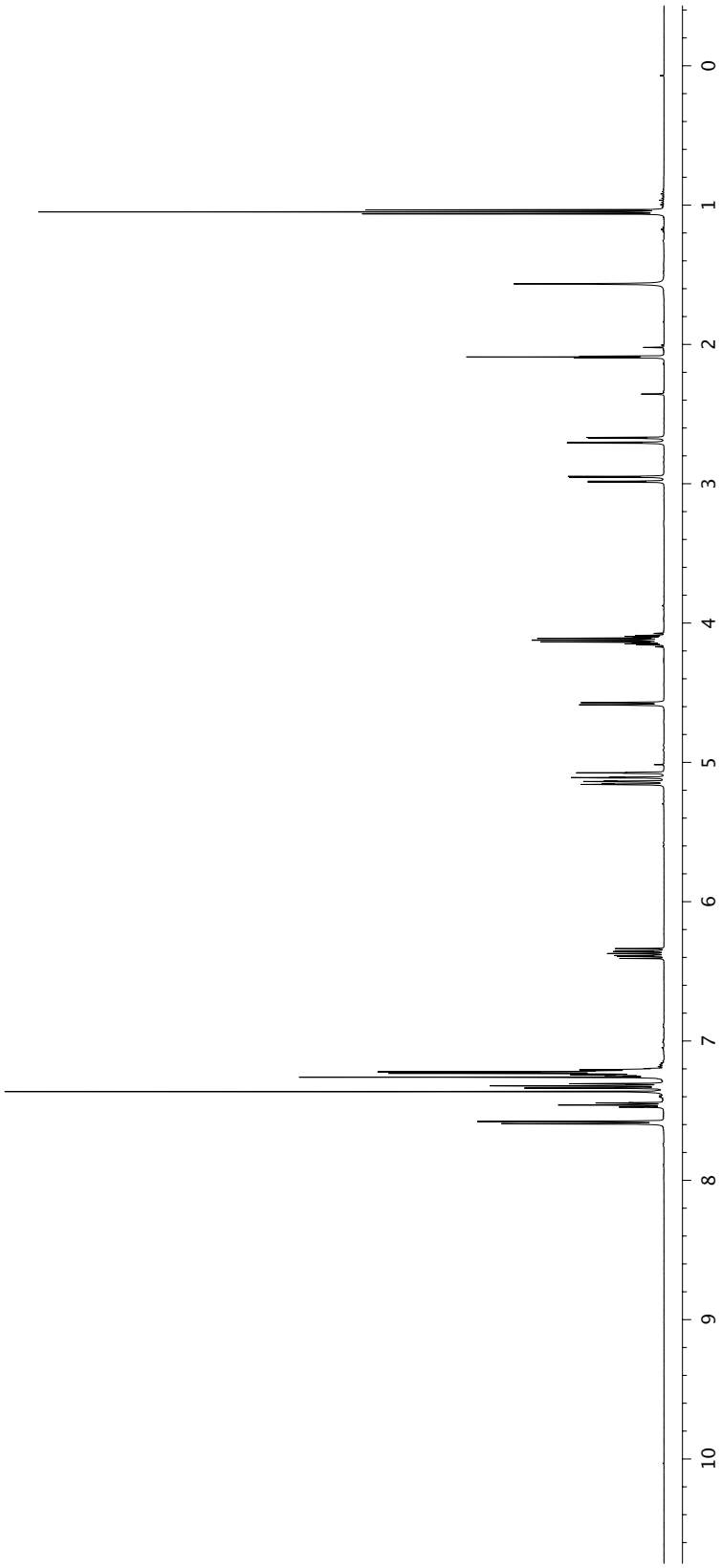


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**.

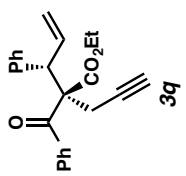


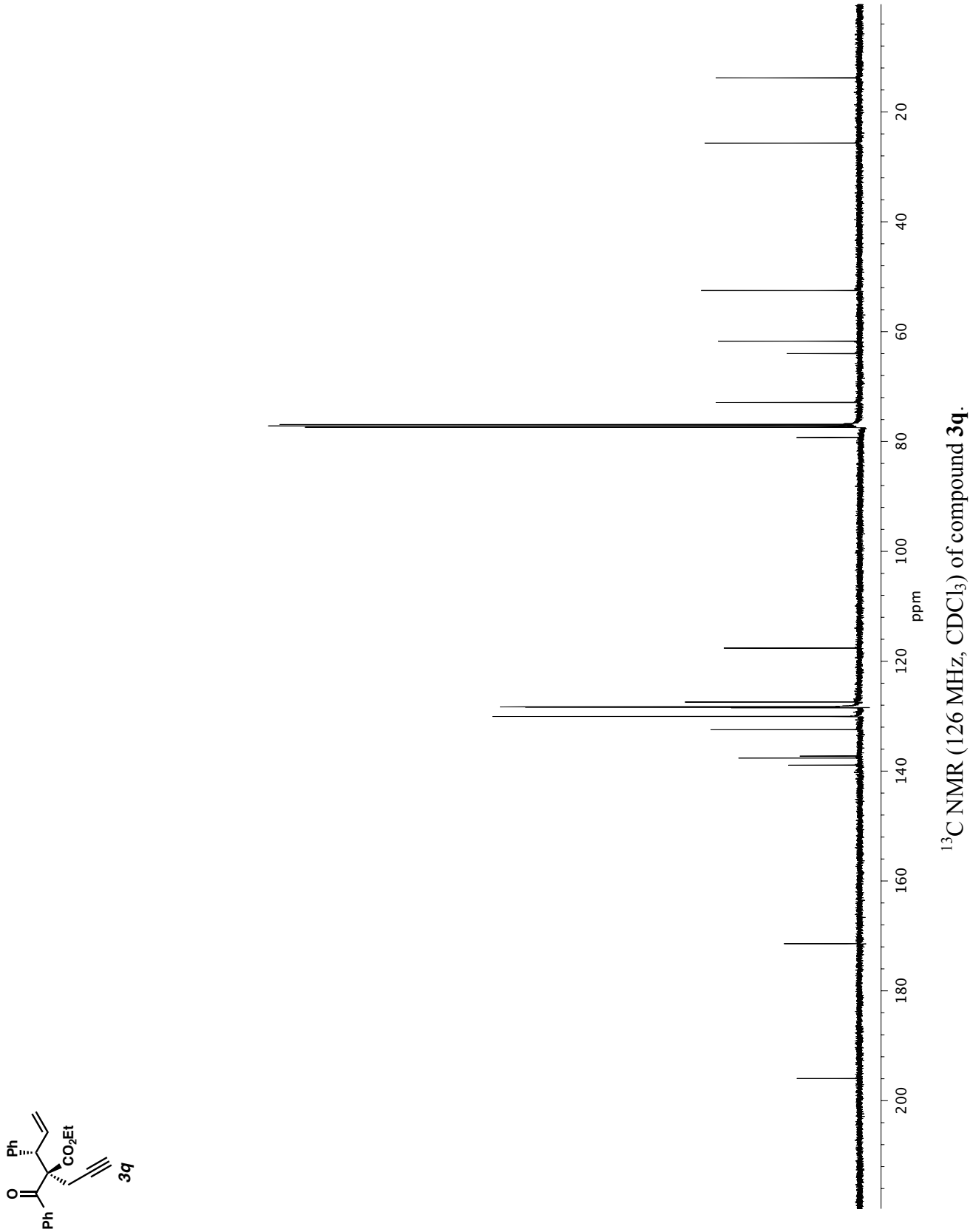


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3p**.

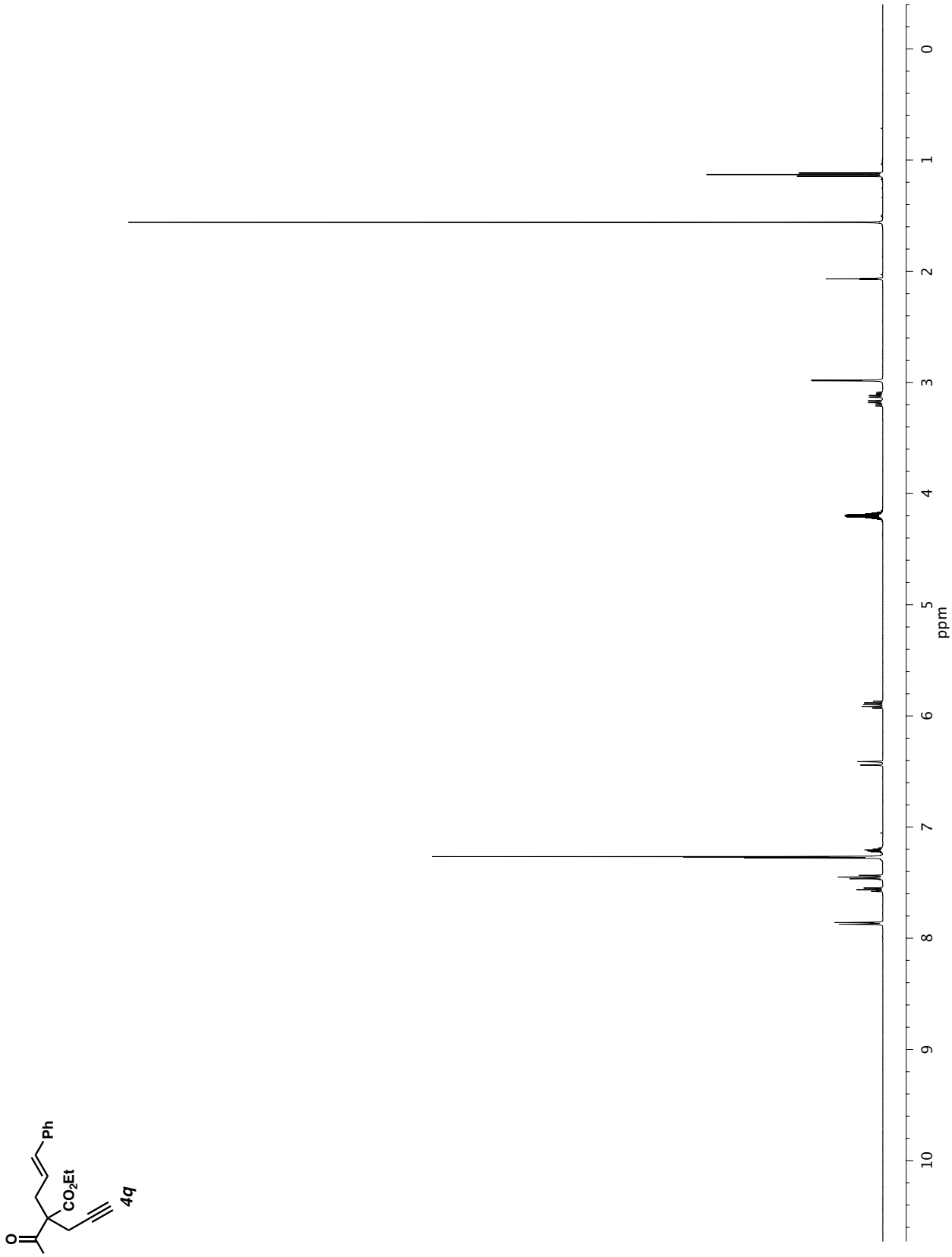


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**.

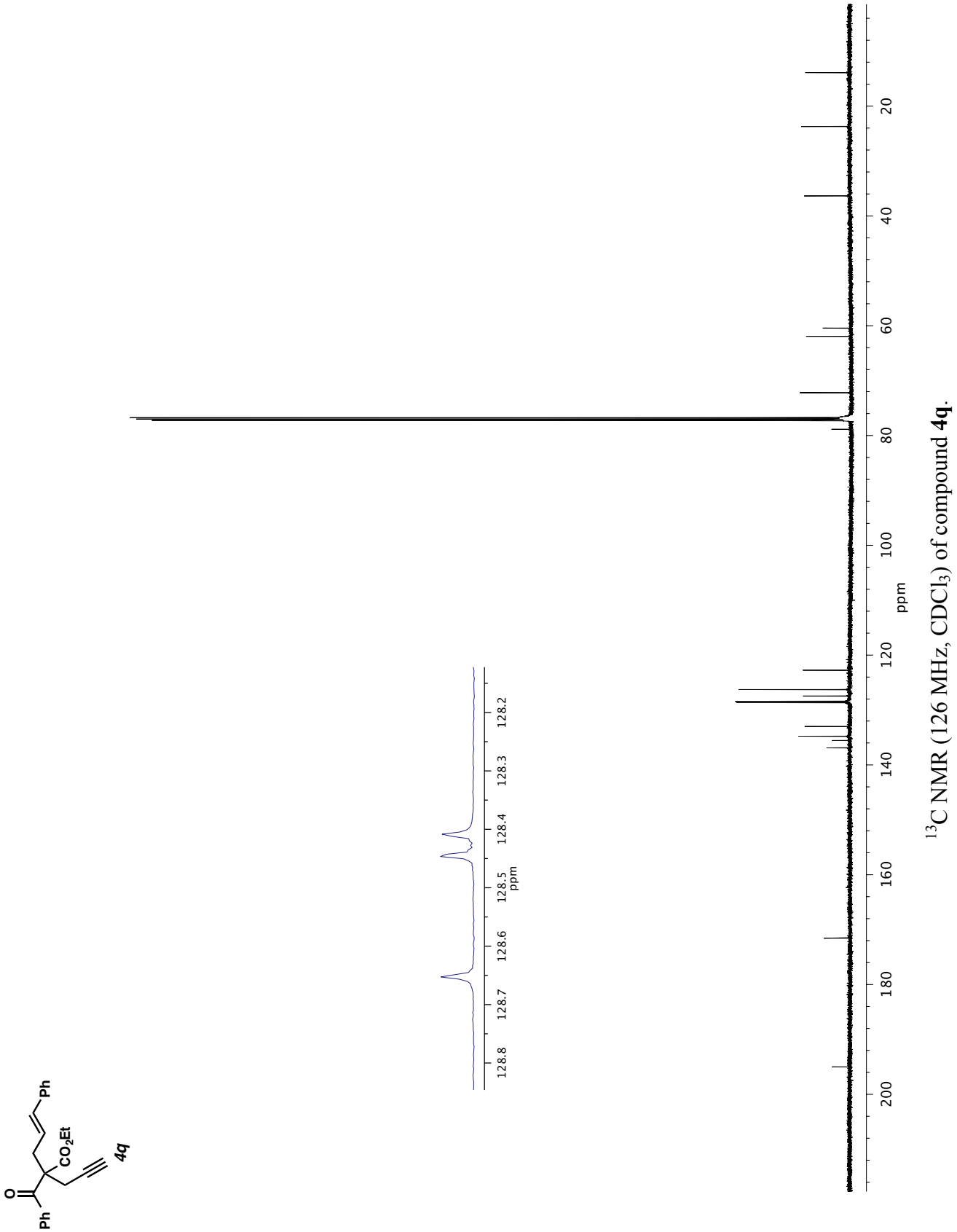




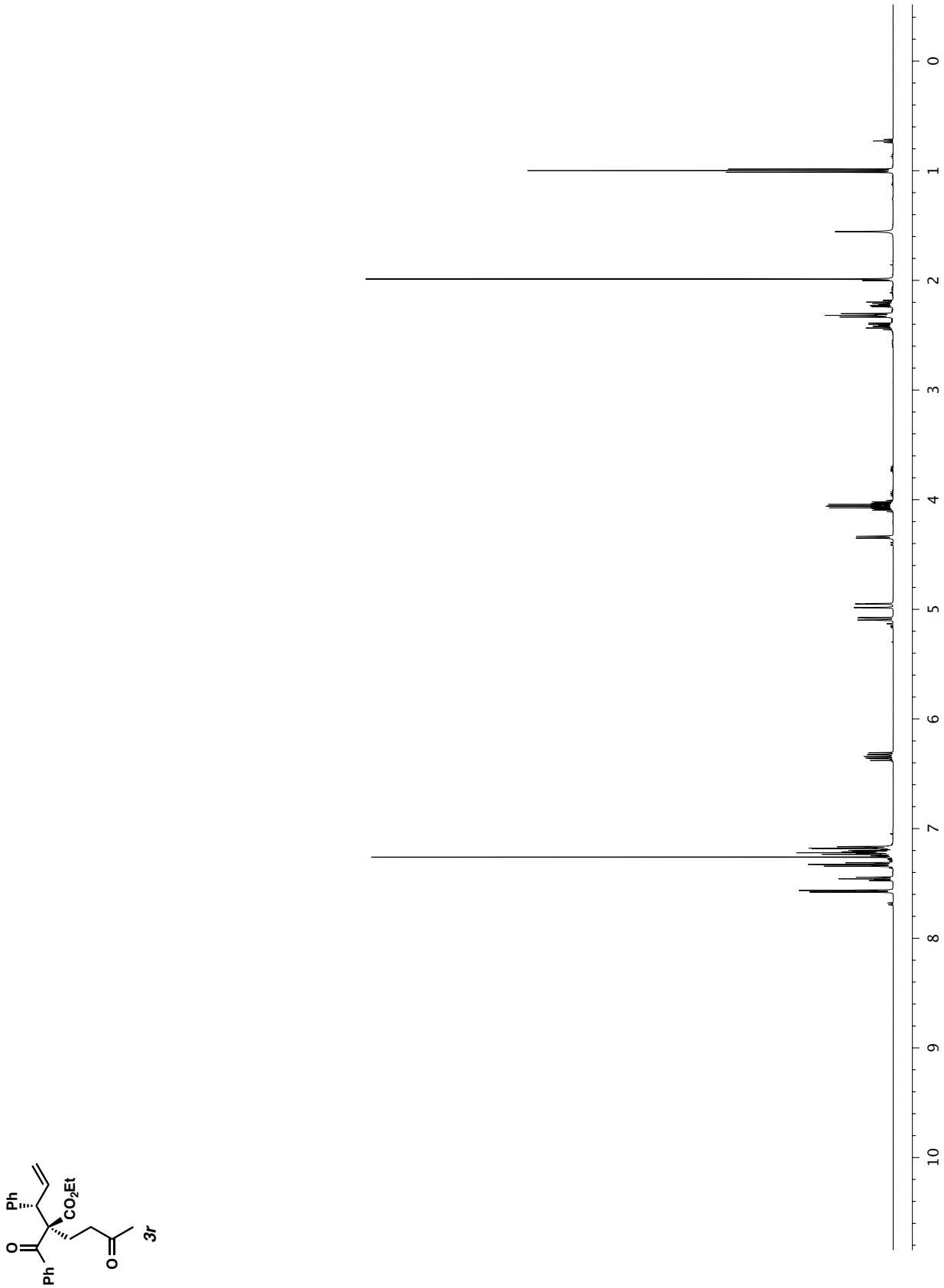
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3q**.



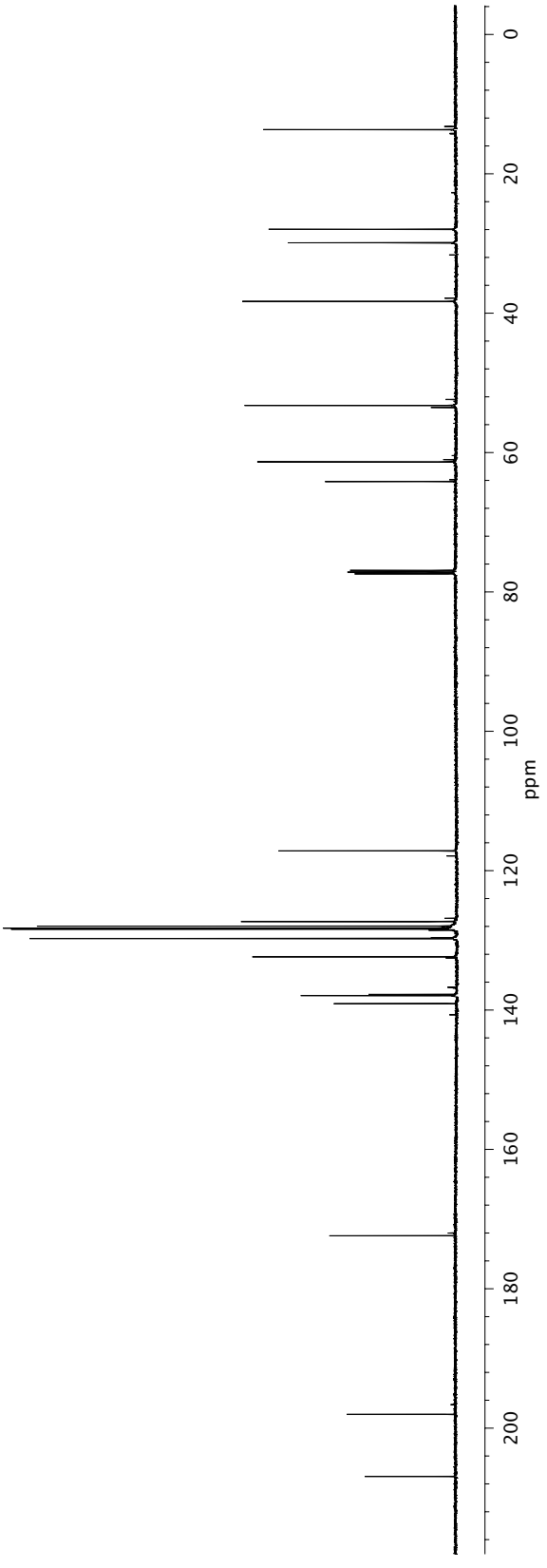
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4q**.



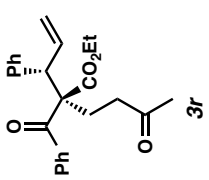
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4q**.

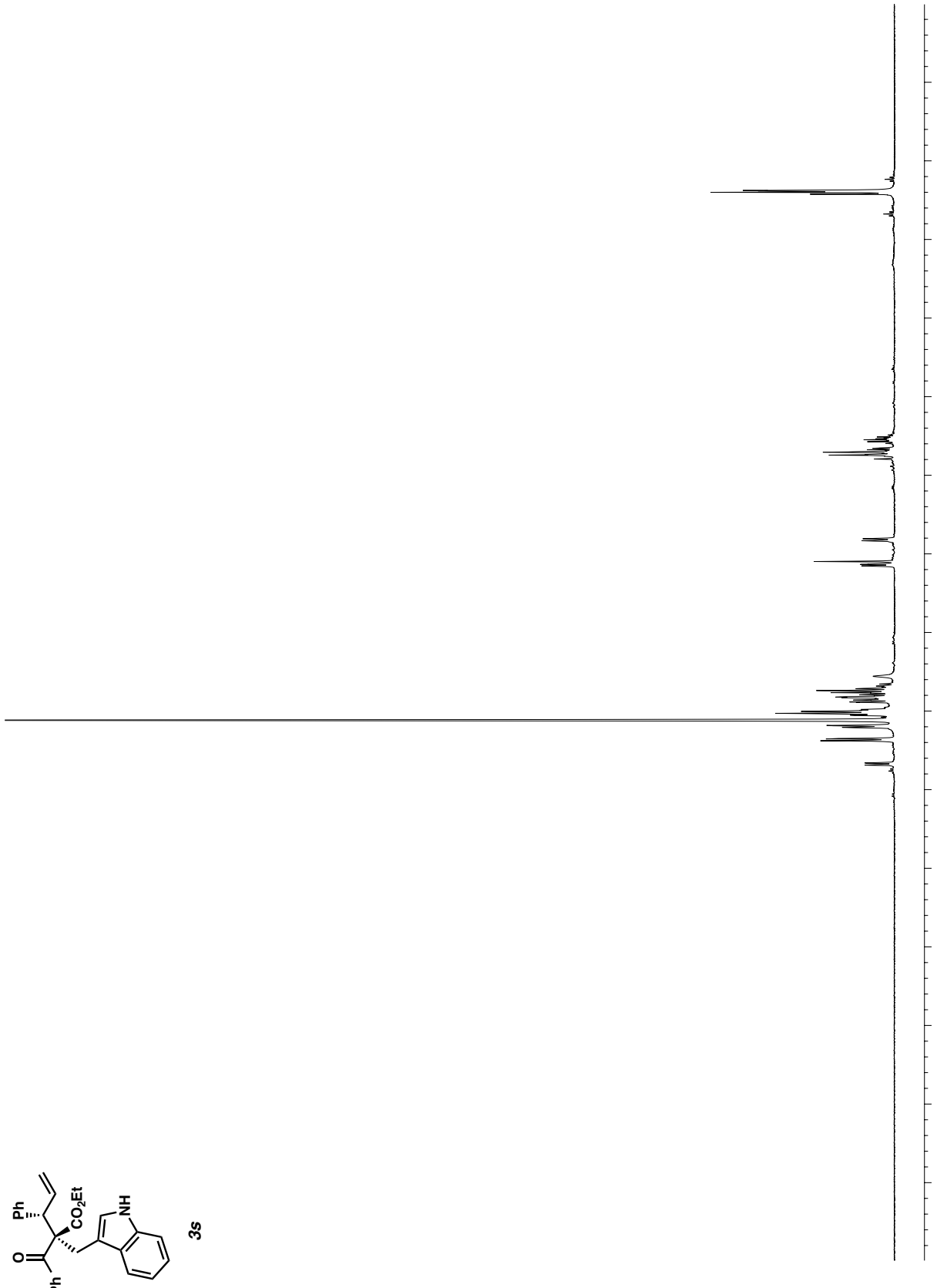


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3r**.

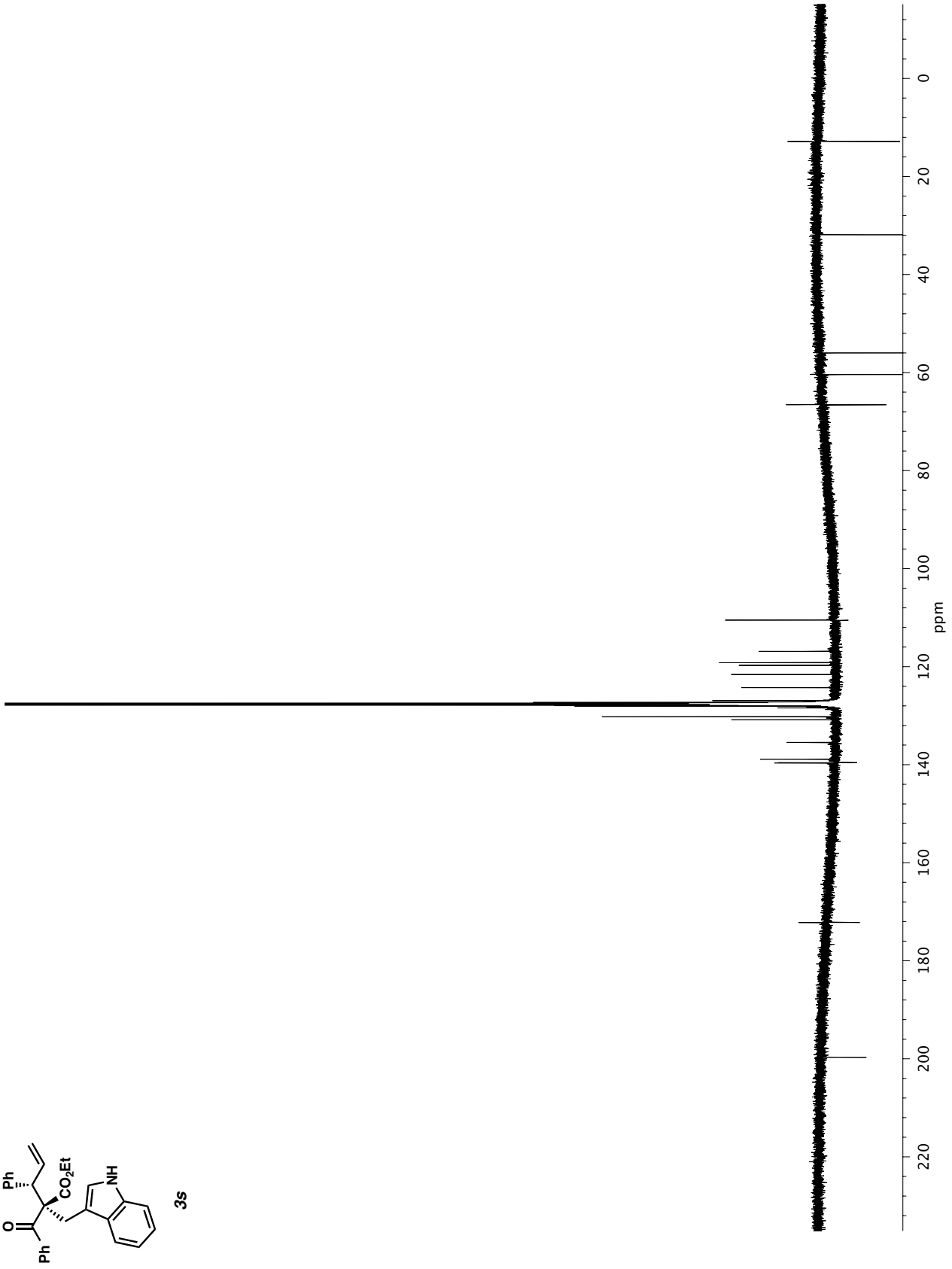


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3r**.

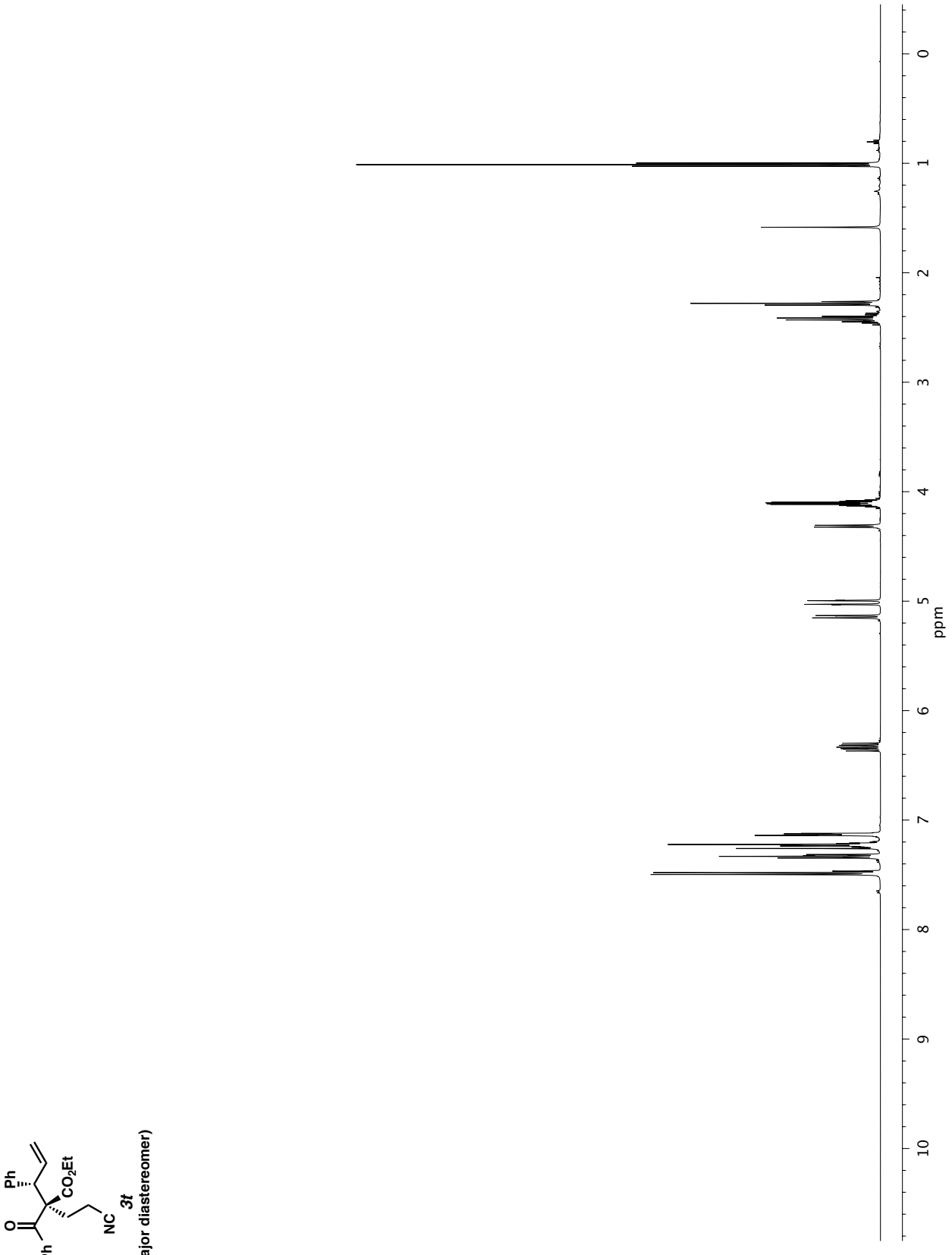




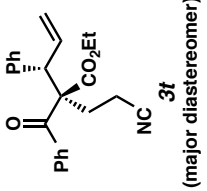
^{1}H NMR (500 MHz, C_6D_6) of compound **3s**.

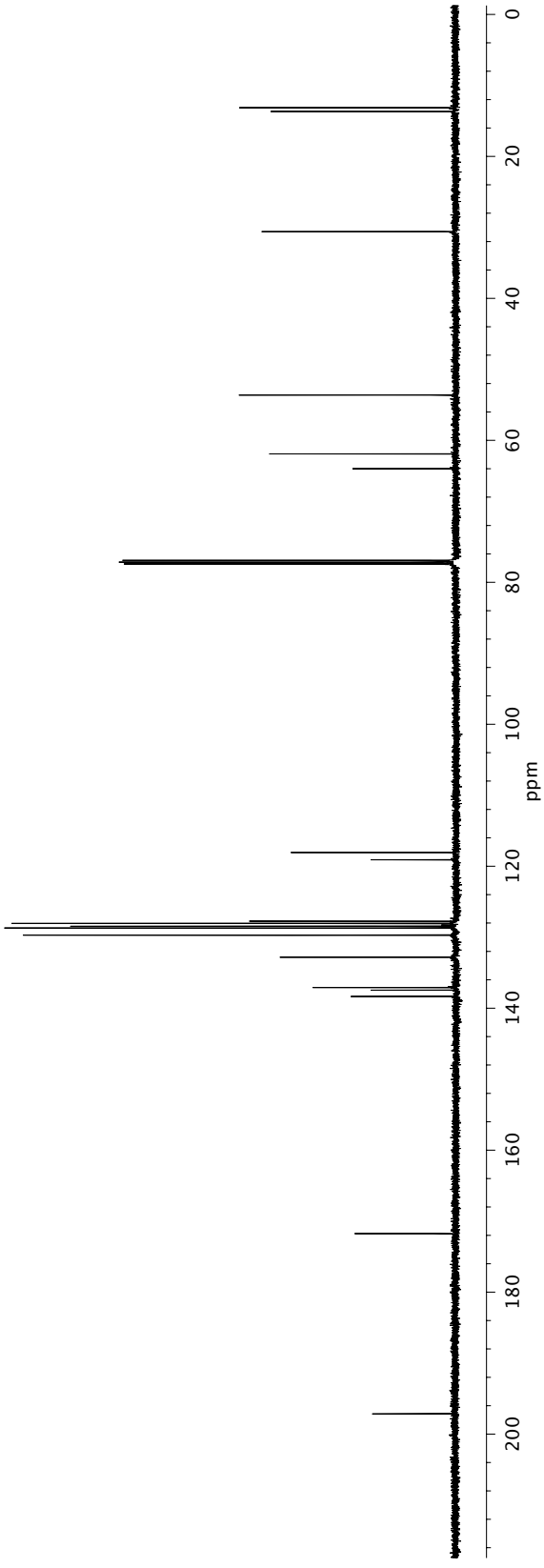


^{13}C NMR (126 MHz, C_6D_6) of compound **3s**.

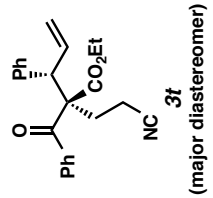


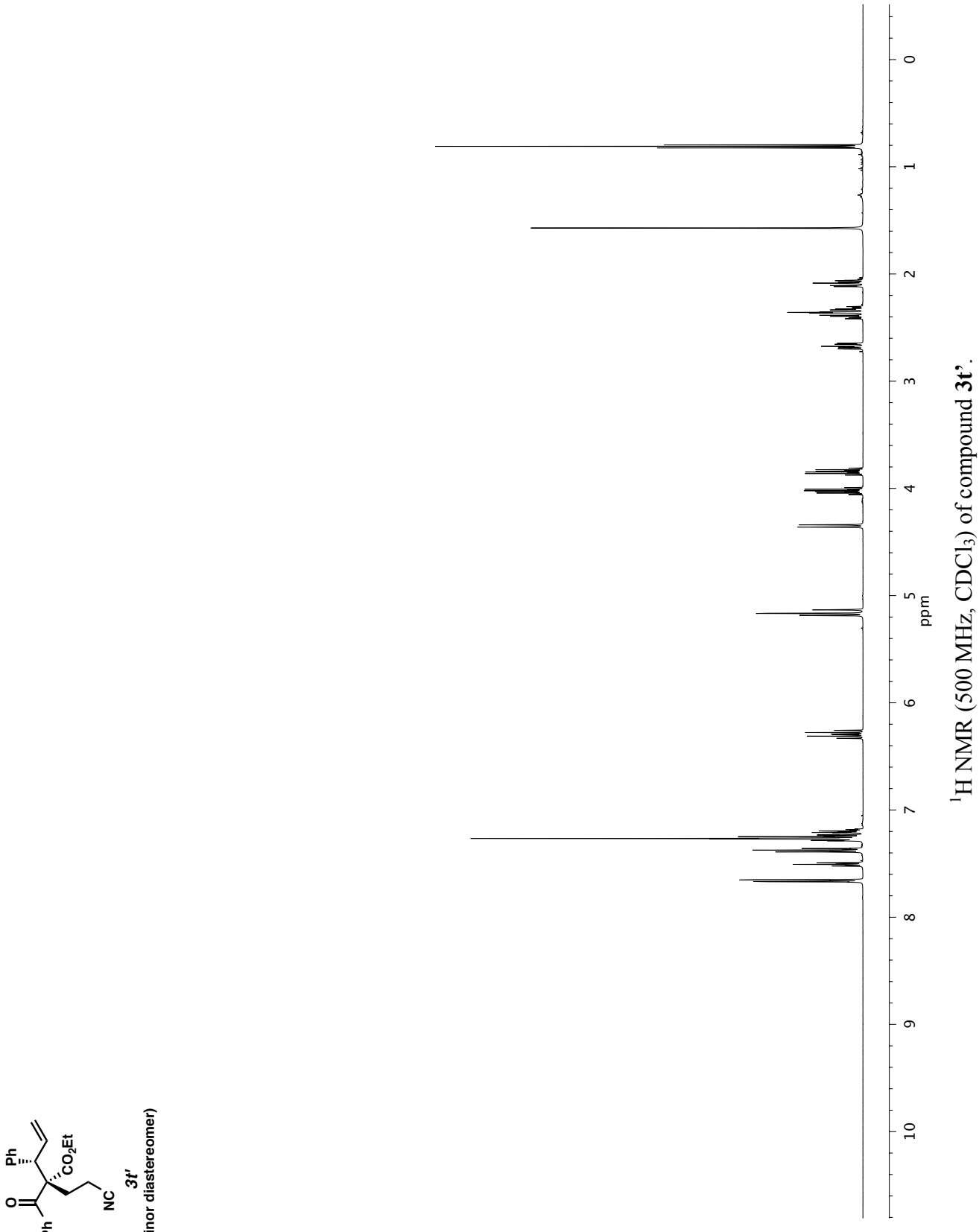
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t**.



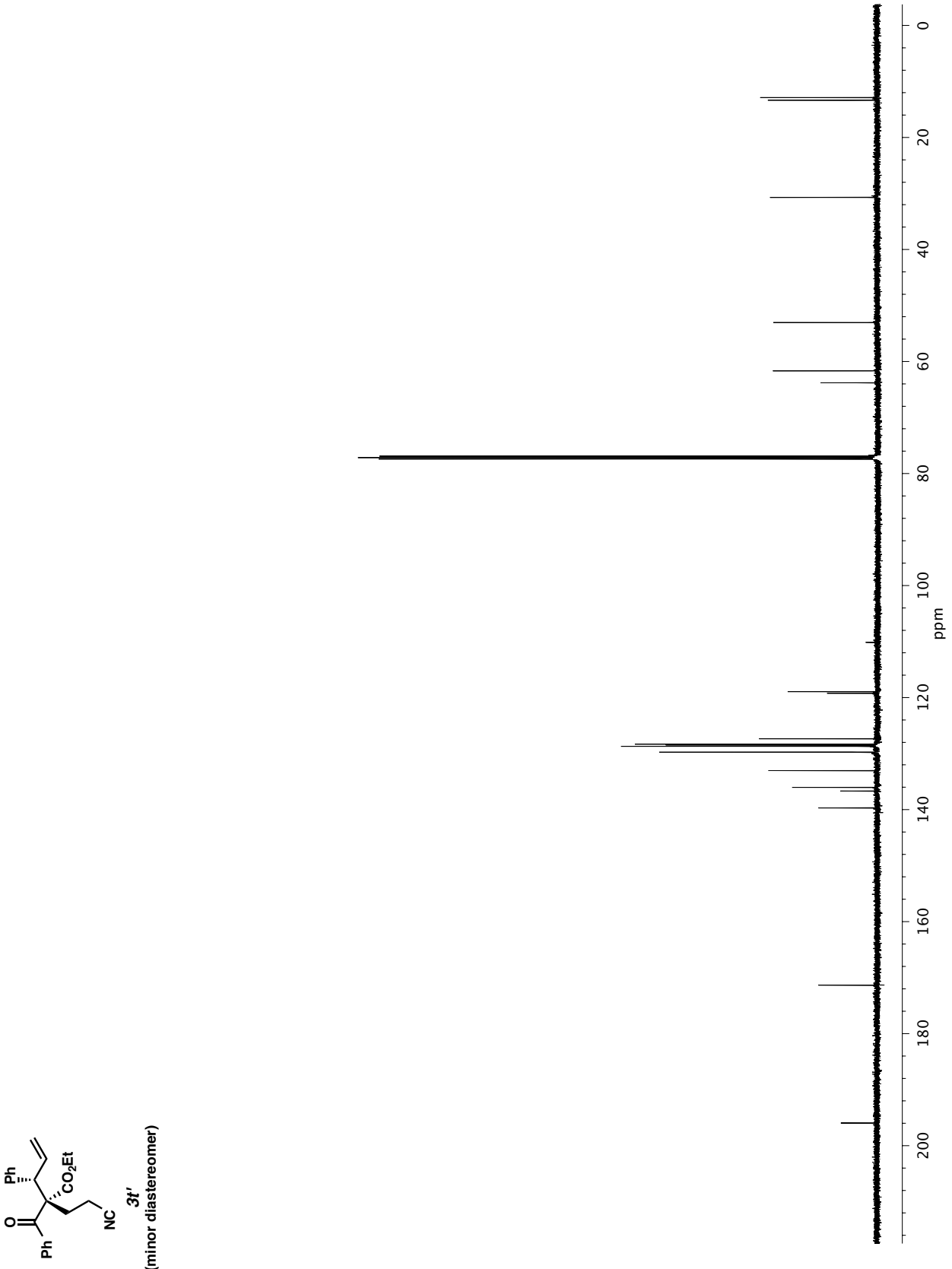


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3t**.

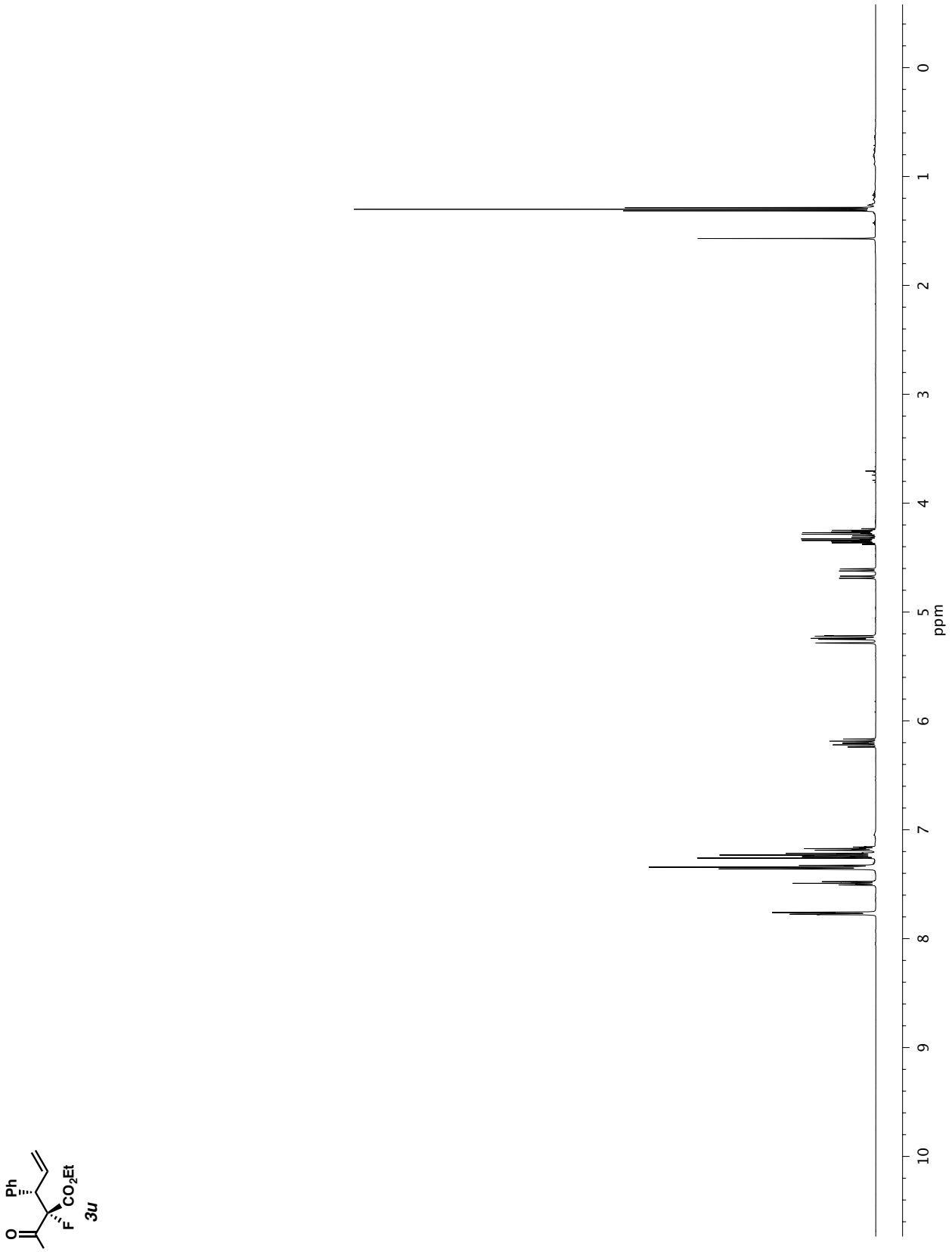




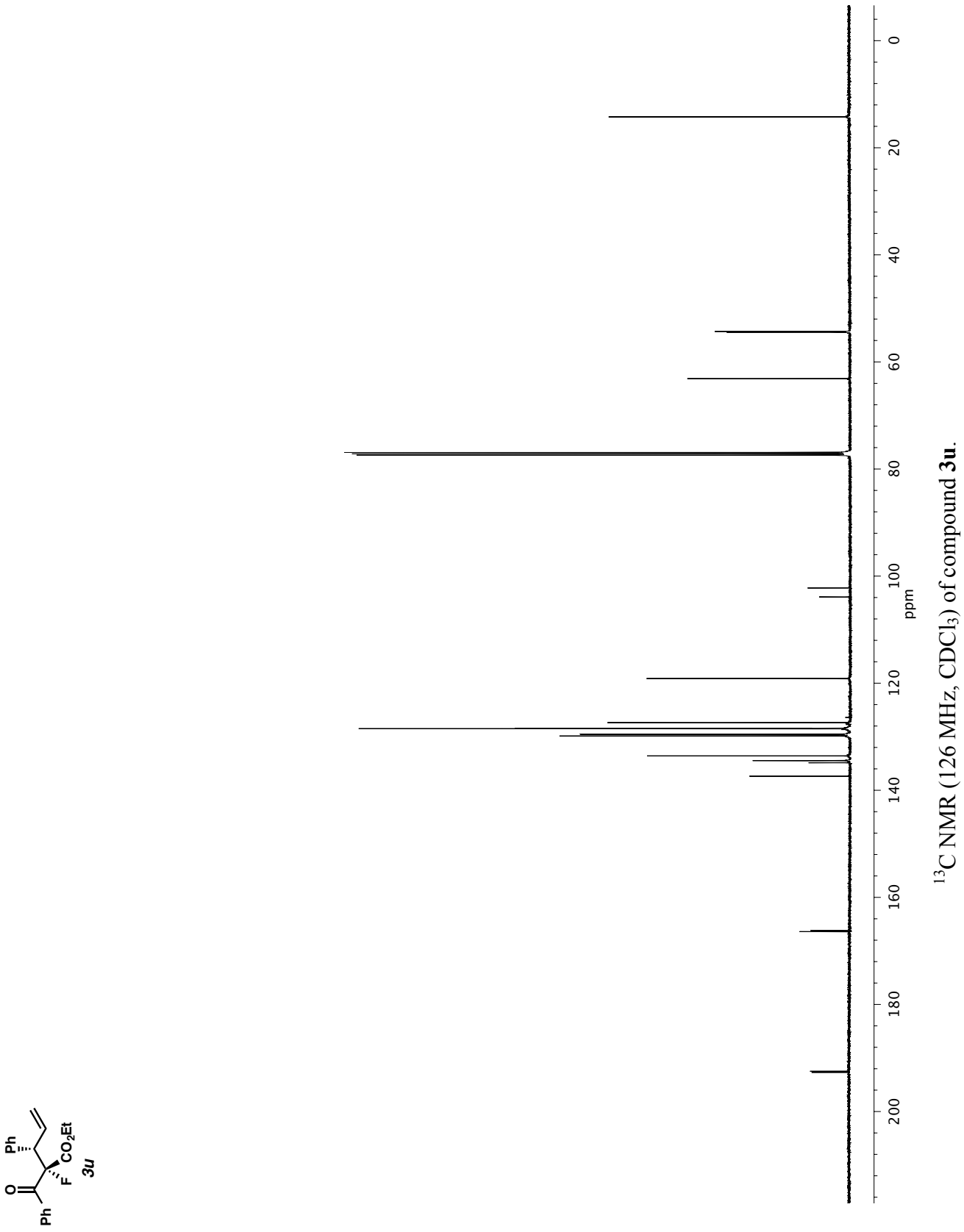
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t'**.



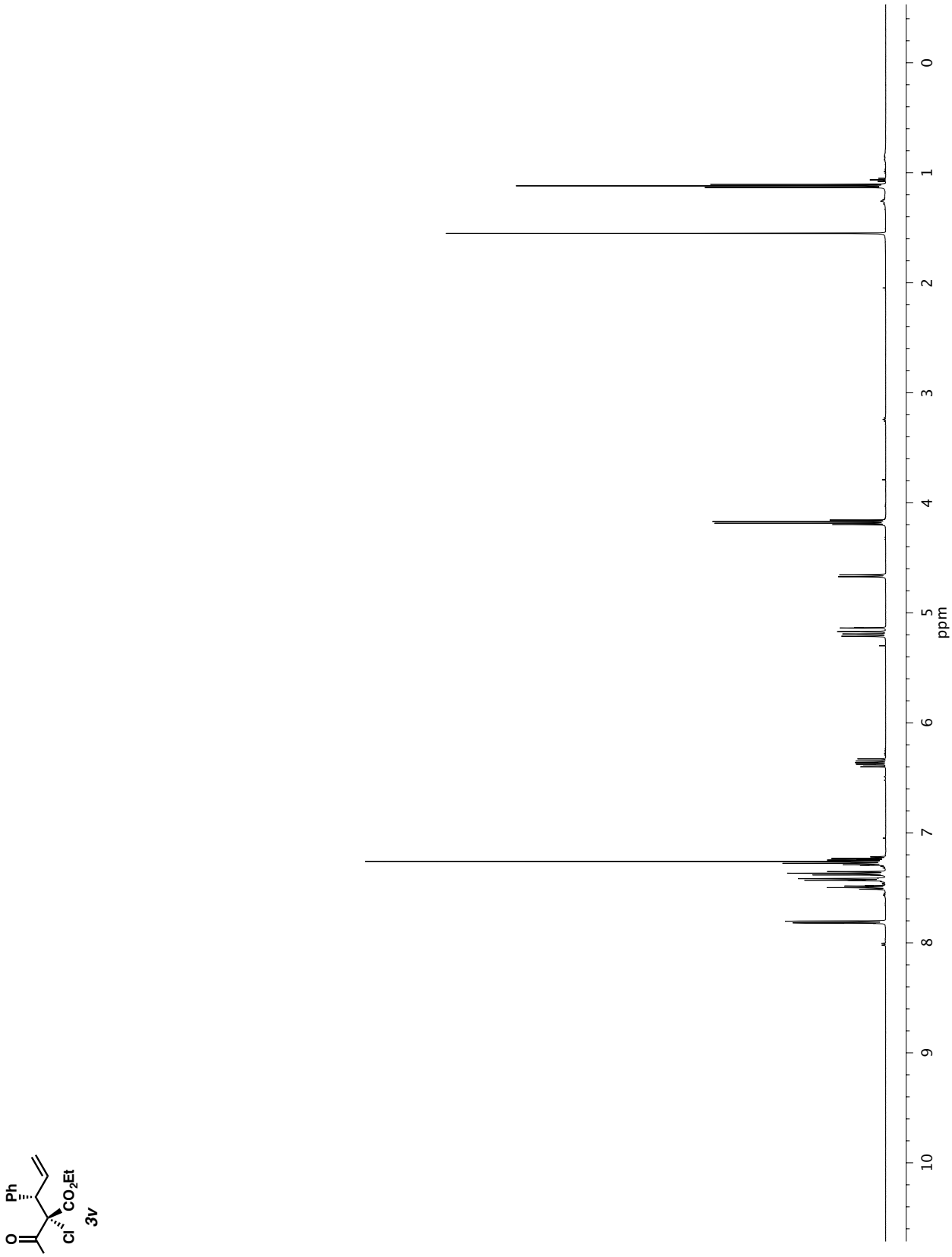
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3 t'**.



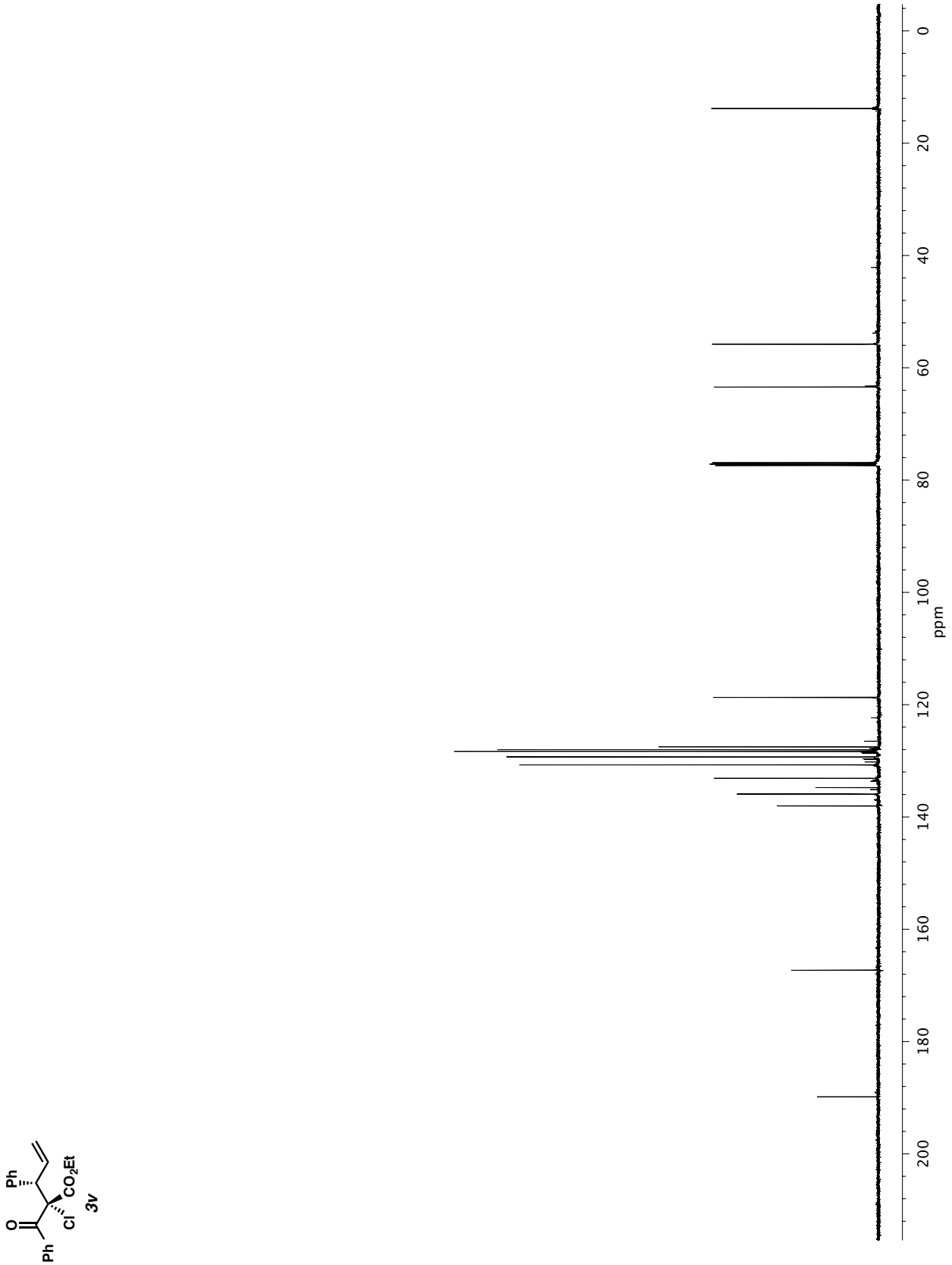
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**.



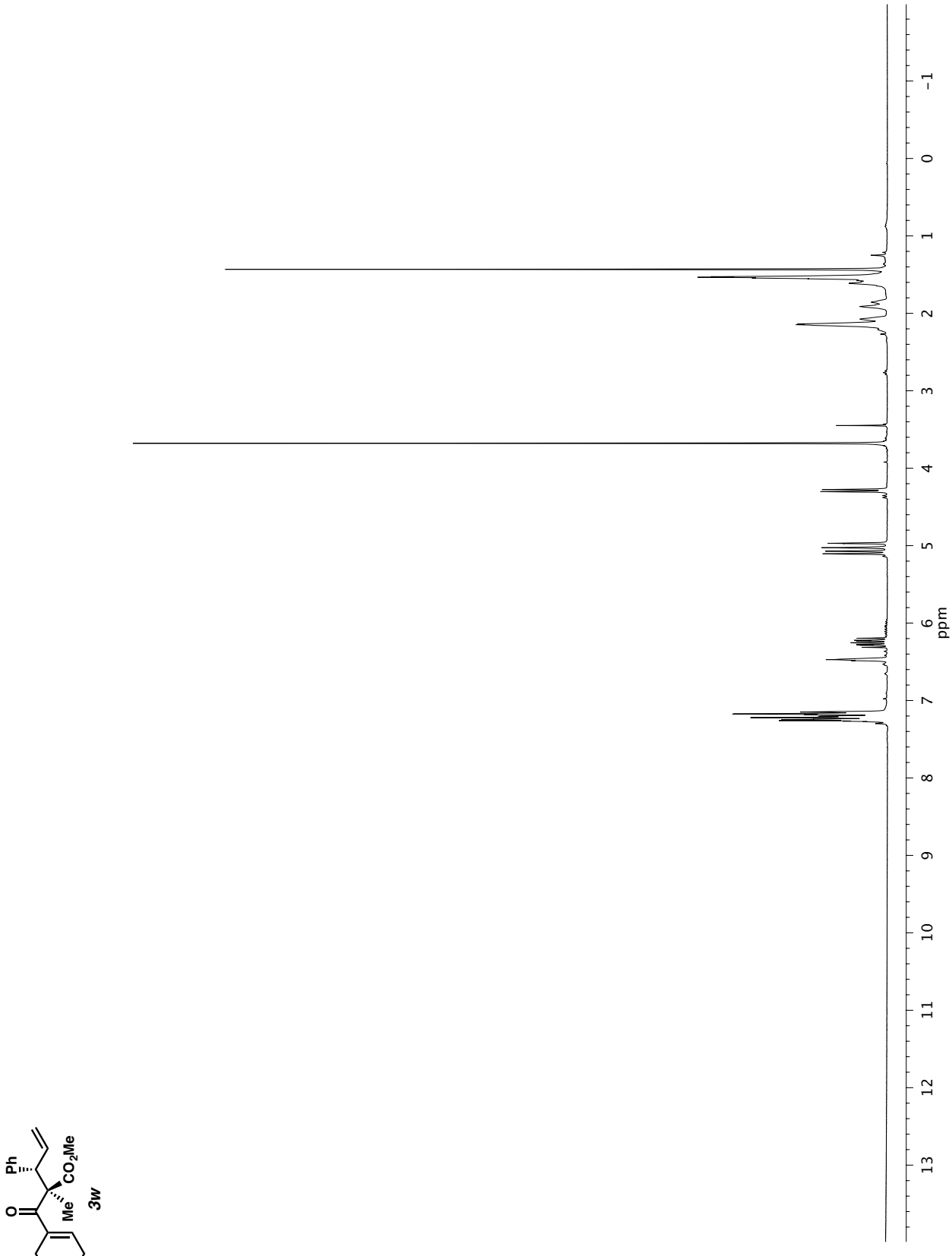
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3u**.



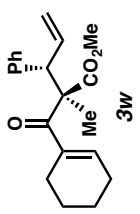
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**.

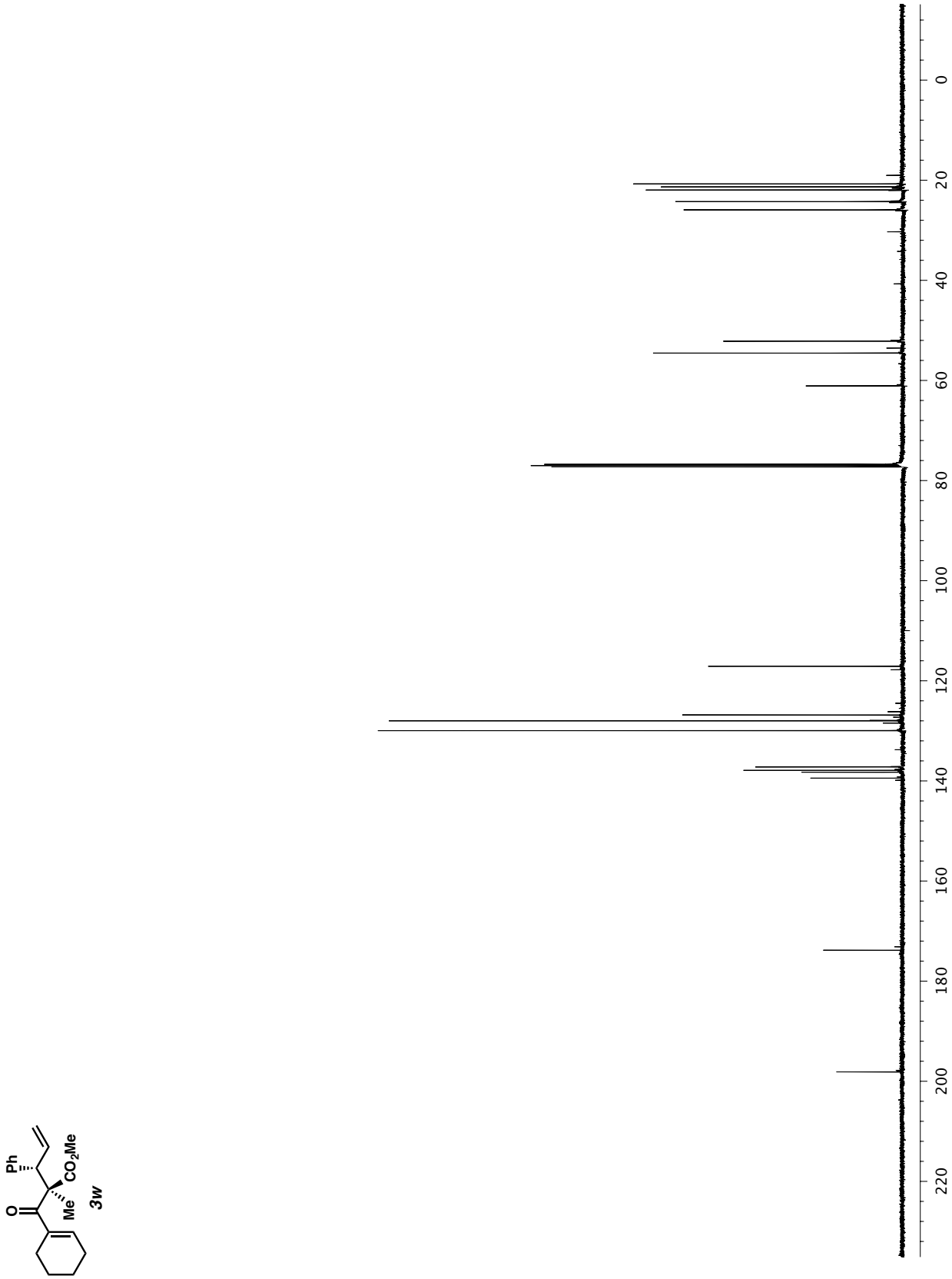


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3v**.

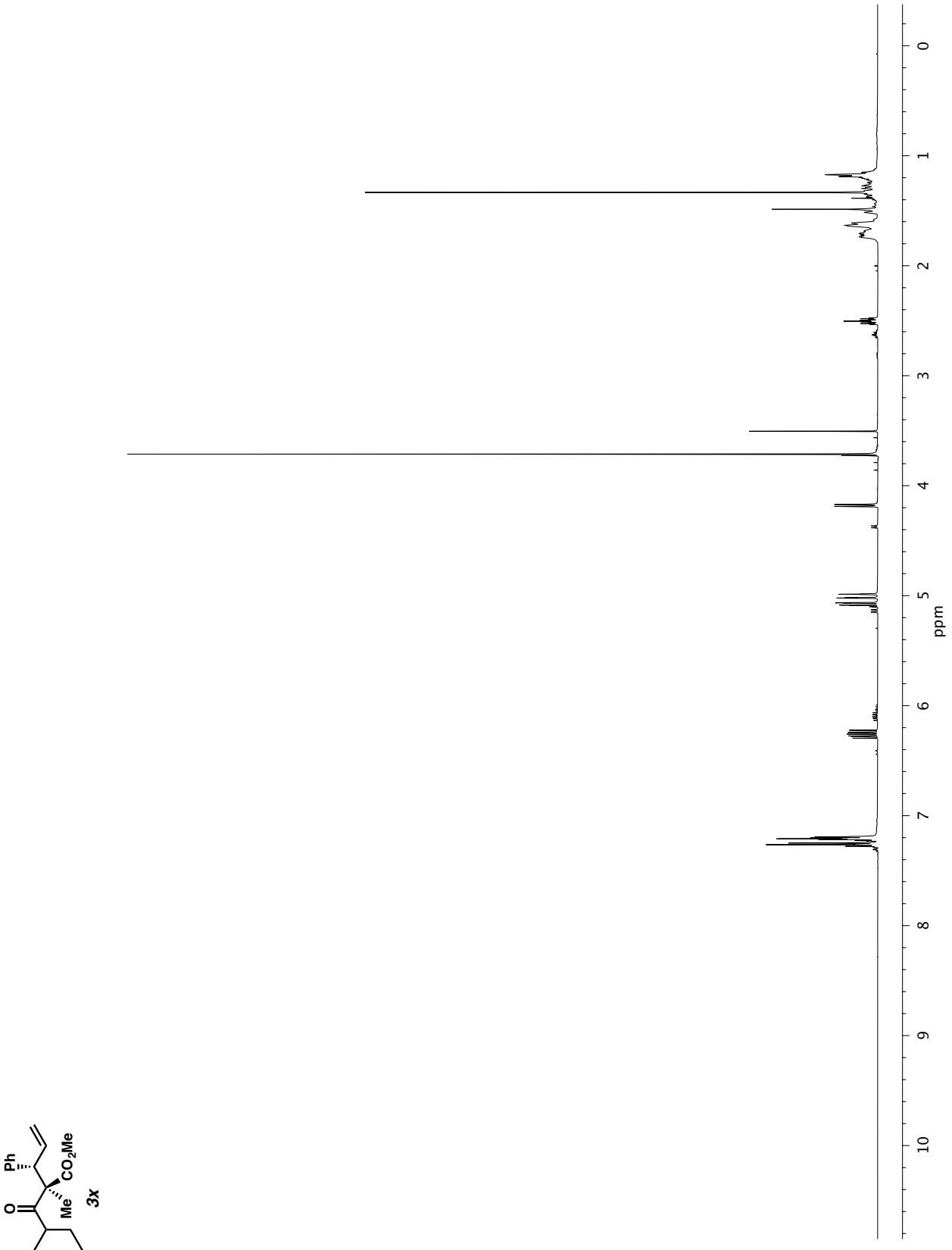


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3w**.

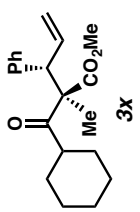


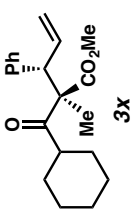


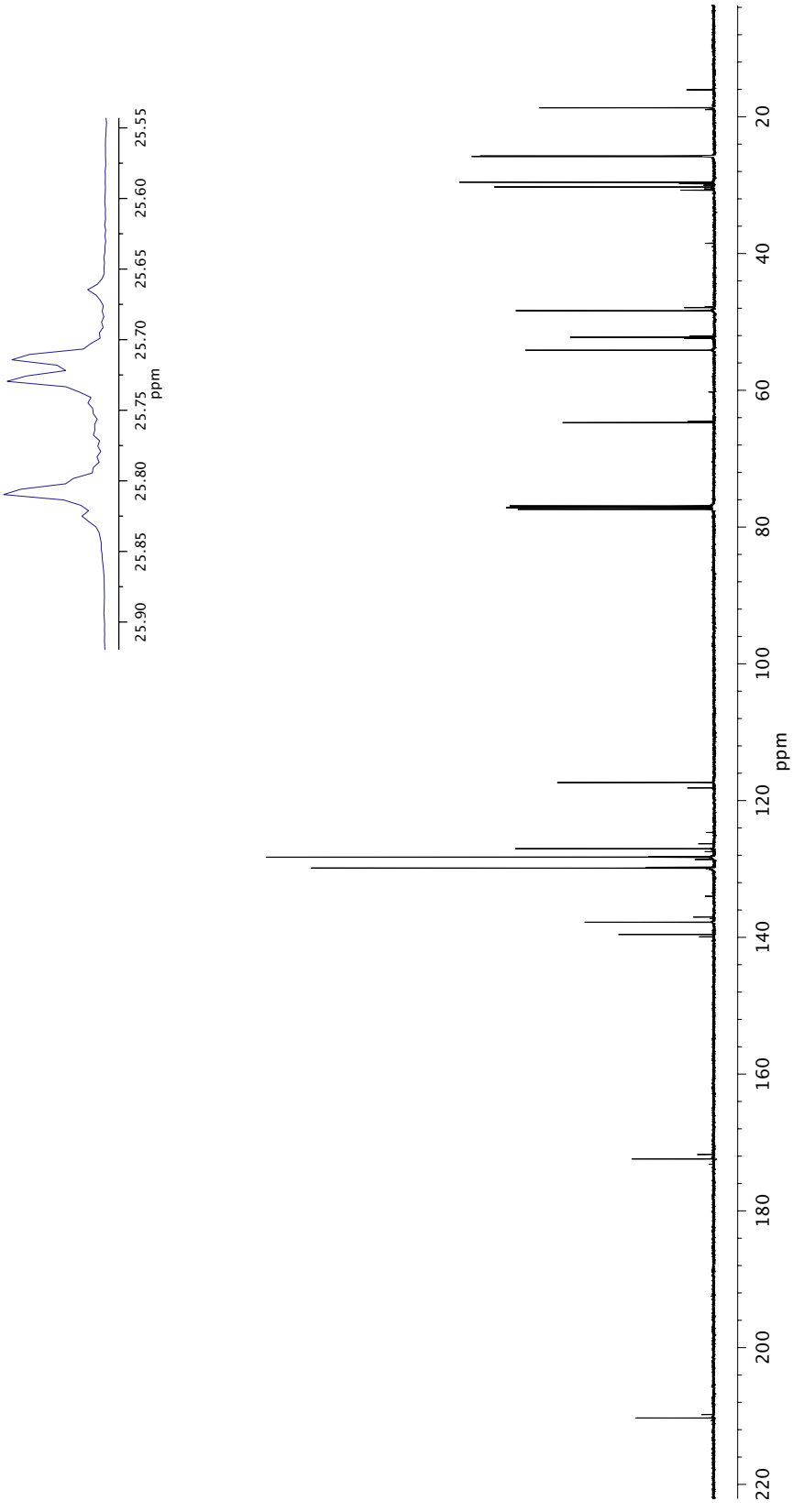
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3w**.



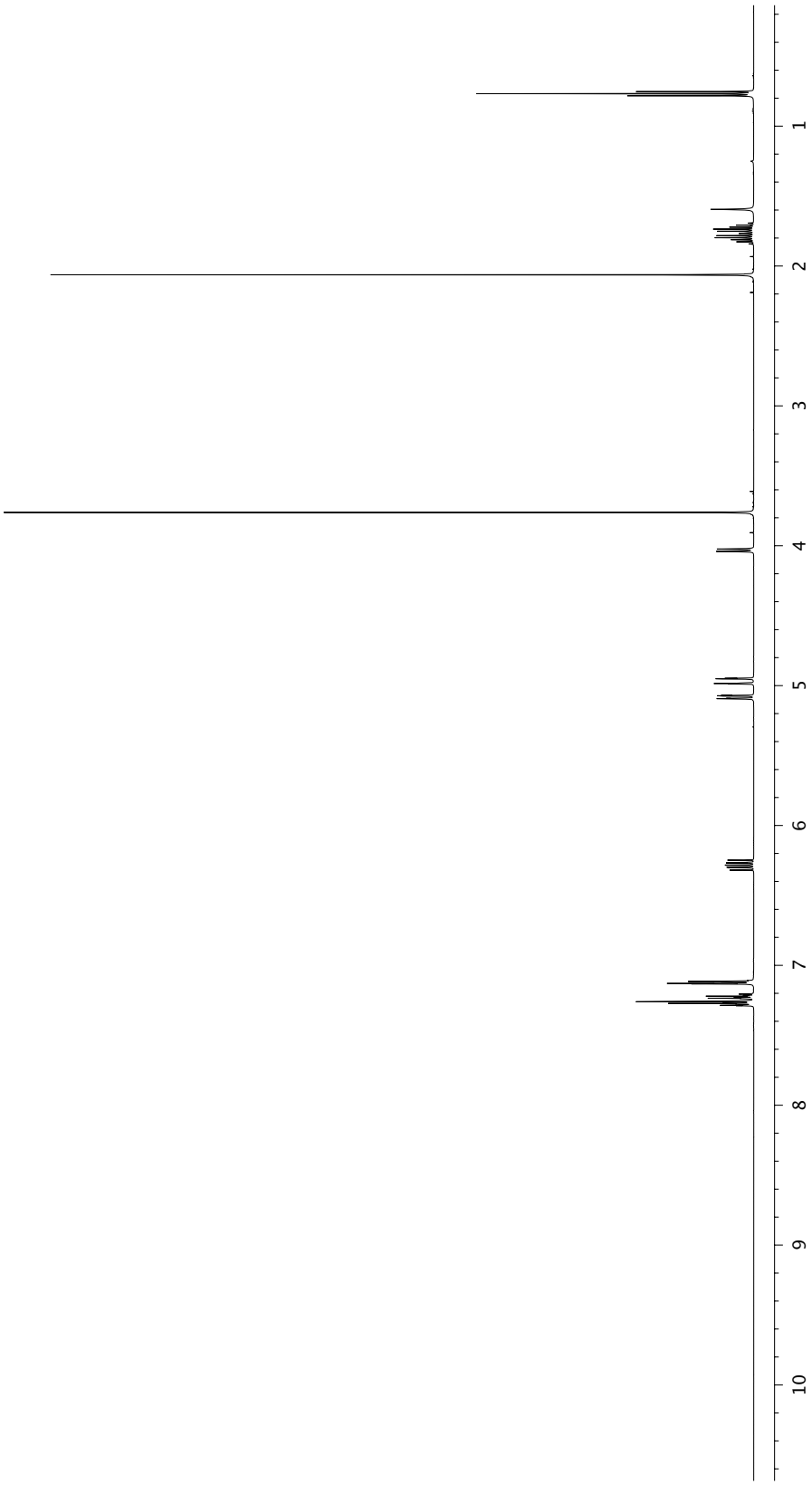
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3x**.



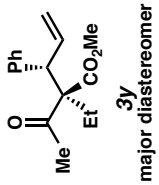




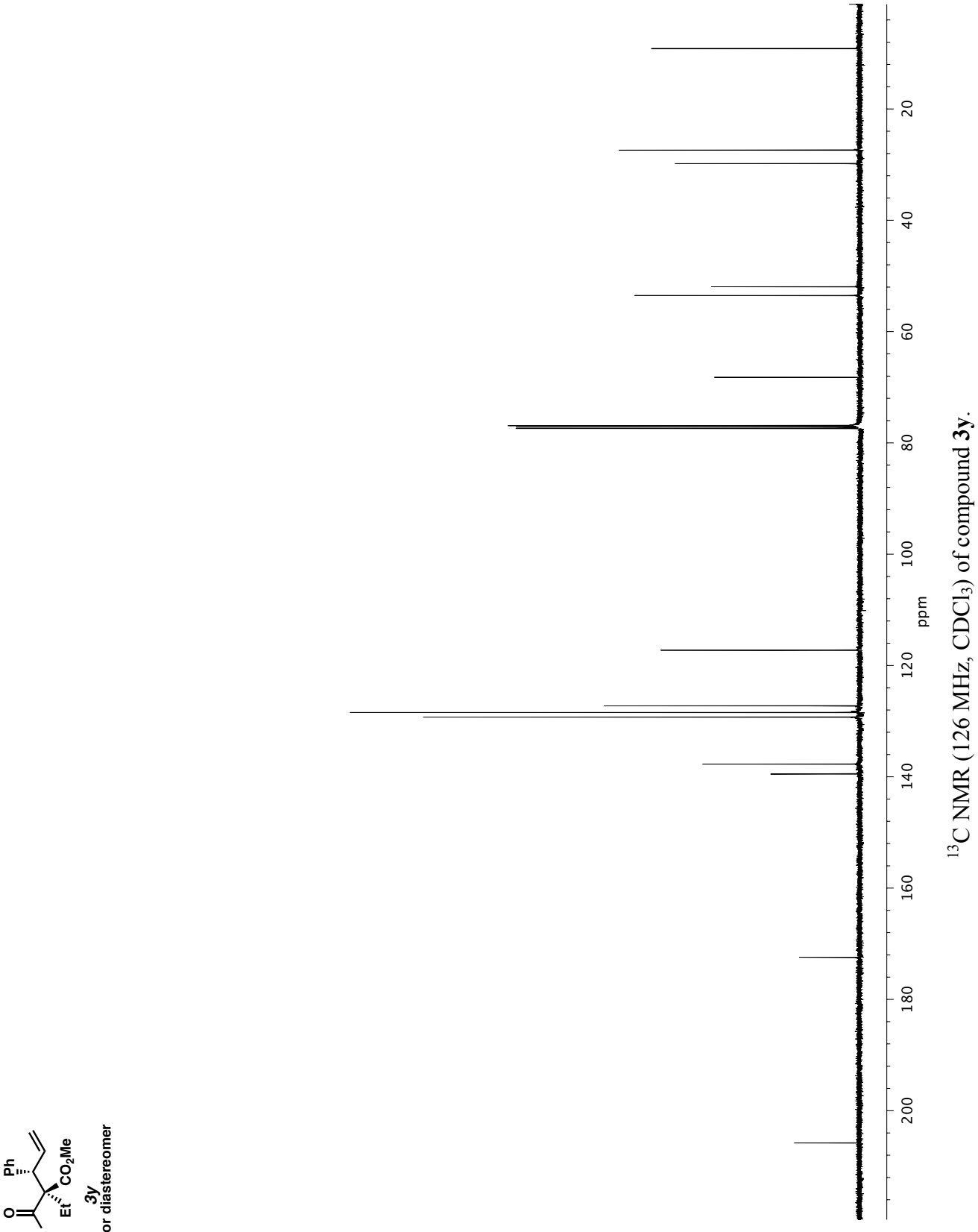
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3x**.



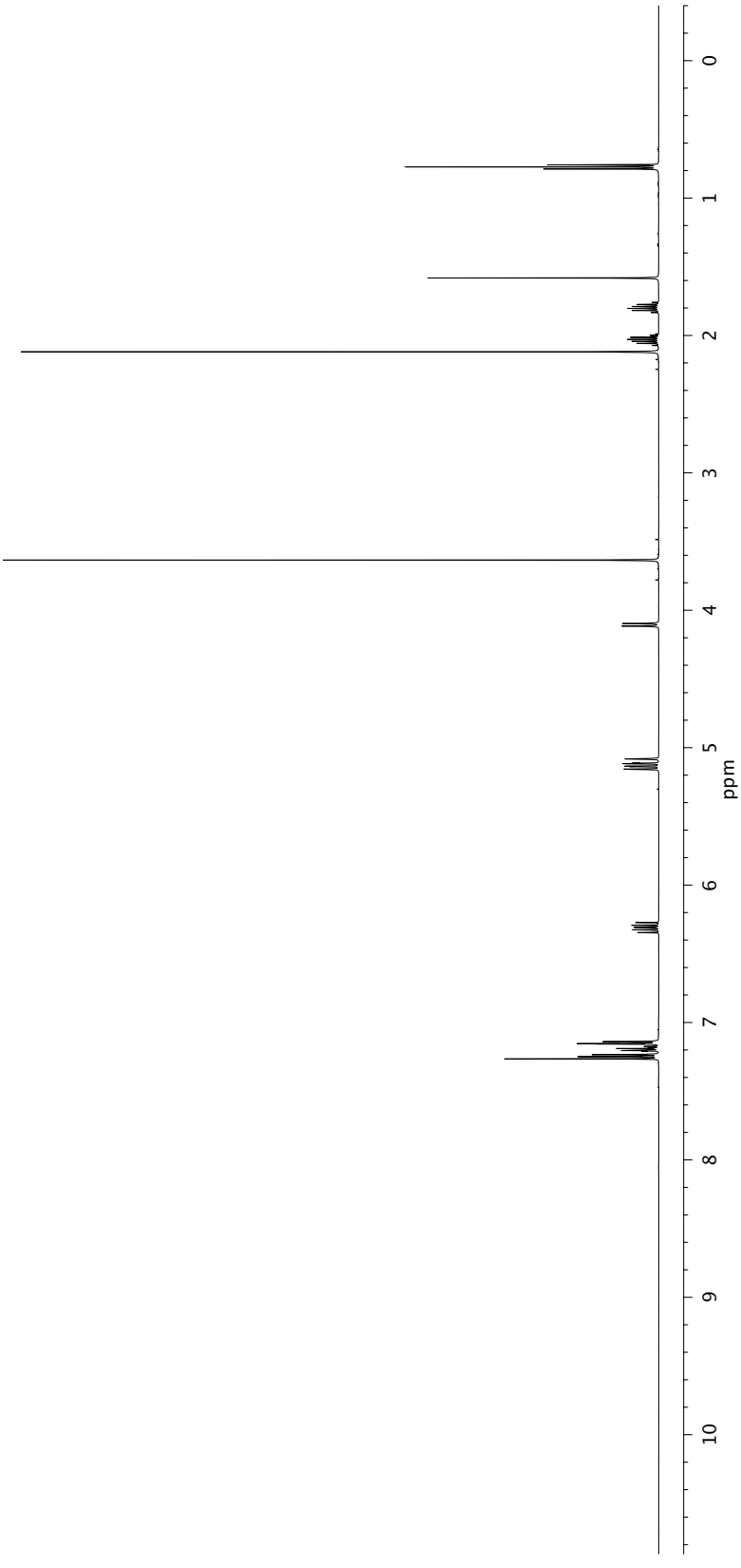
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y**.



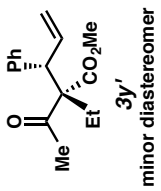
3y
major diastereomer



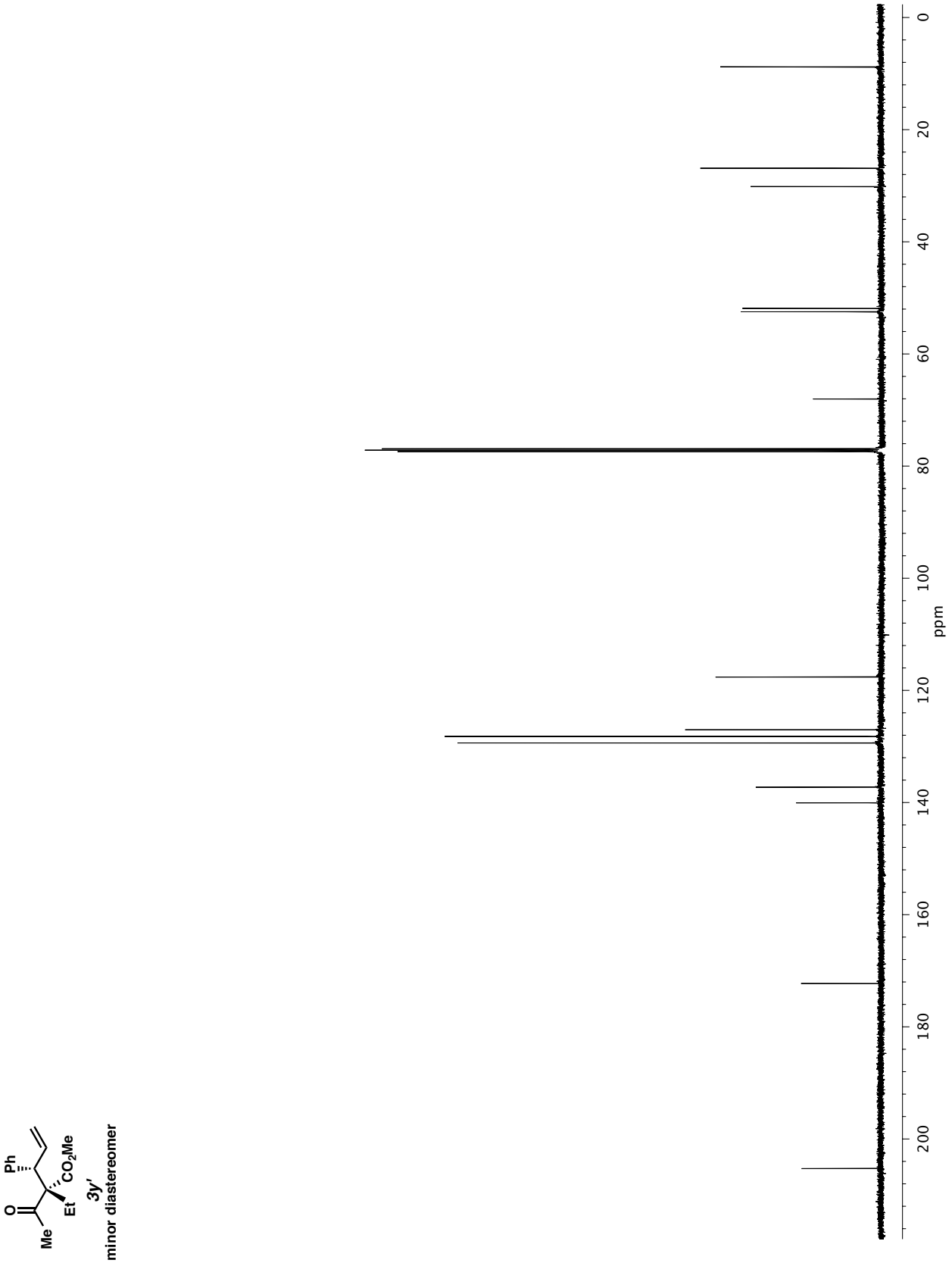
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3y**.



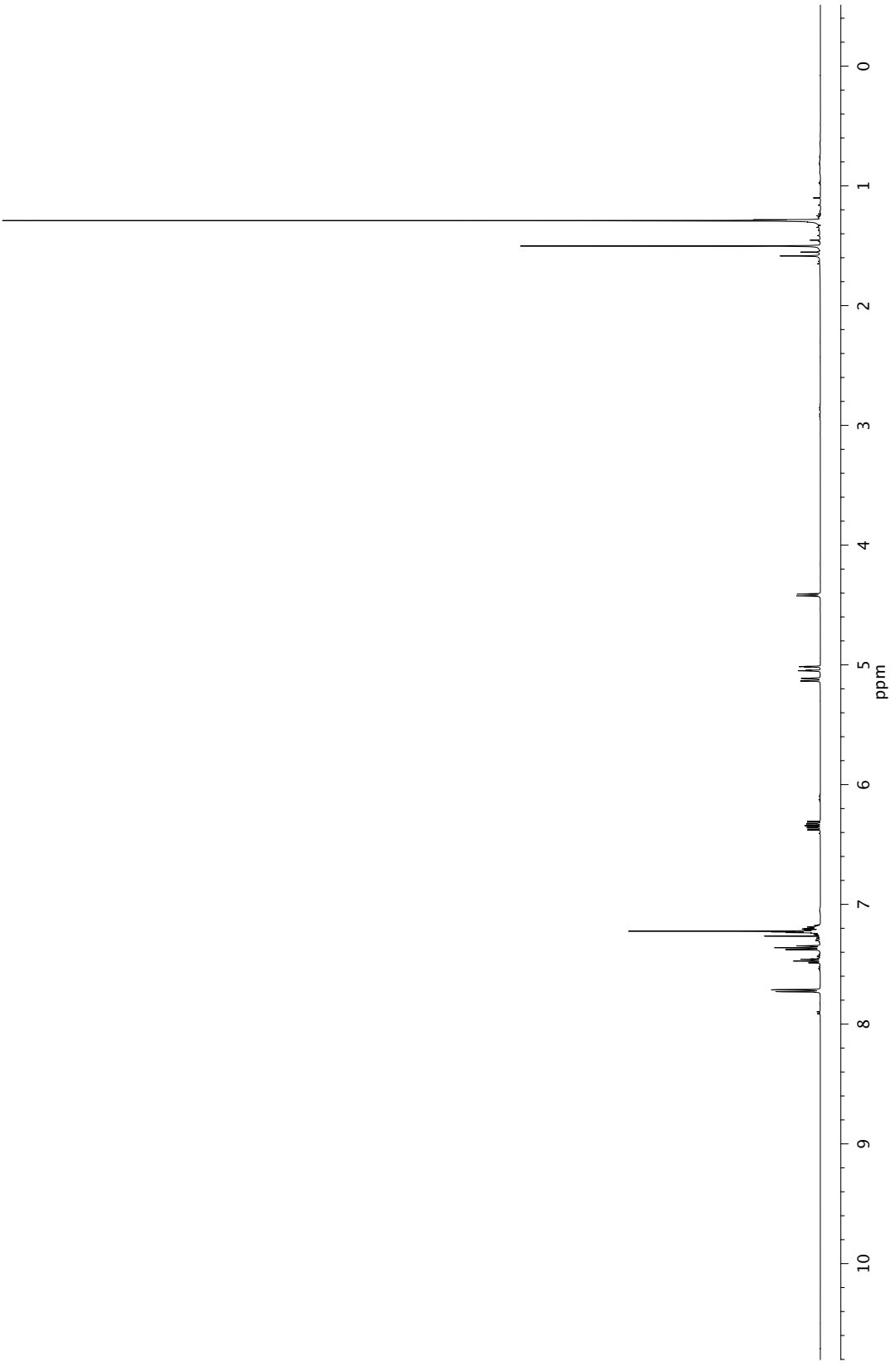
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y'**.



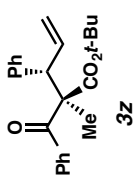
3y'
minor diastereomer



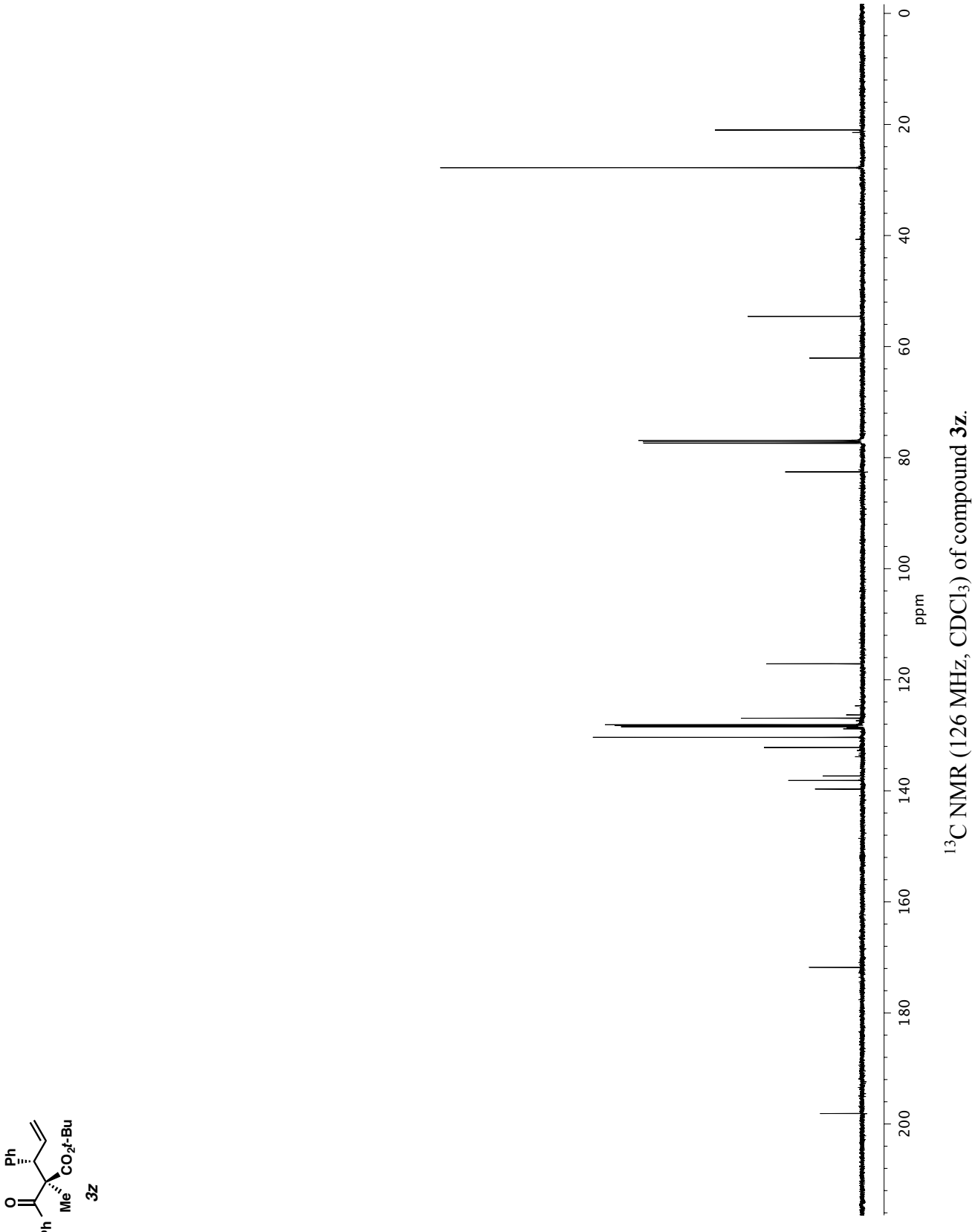
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3y'**.



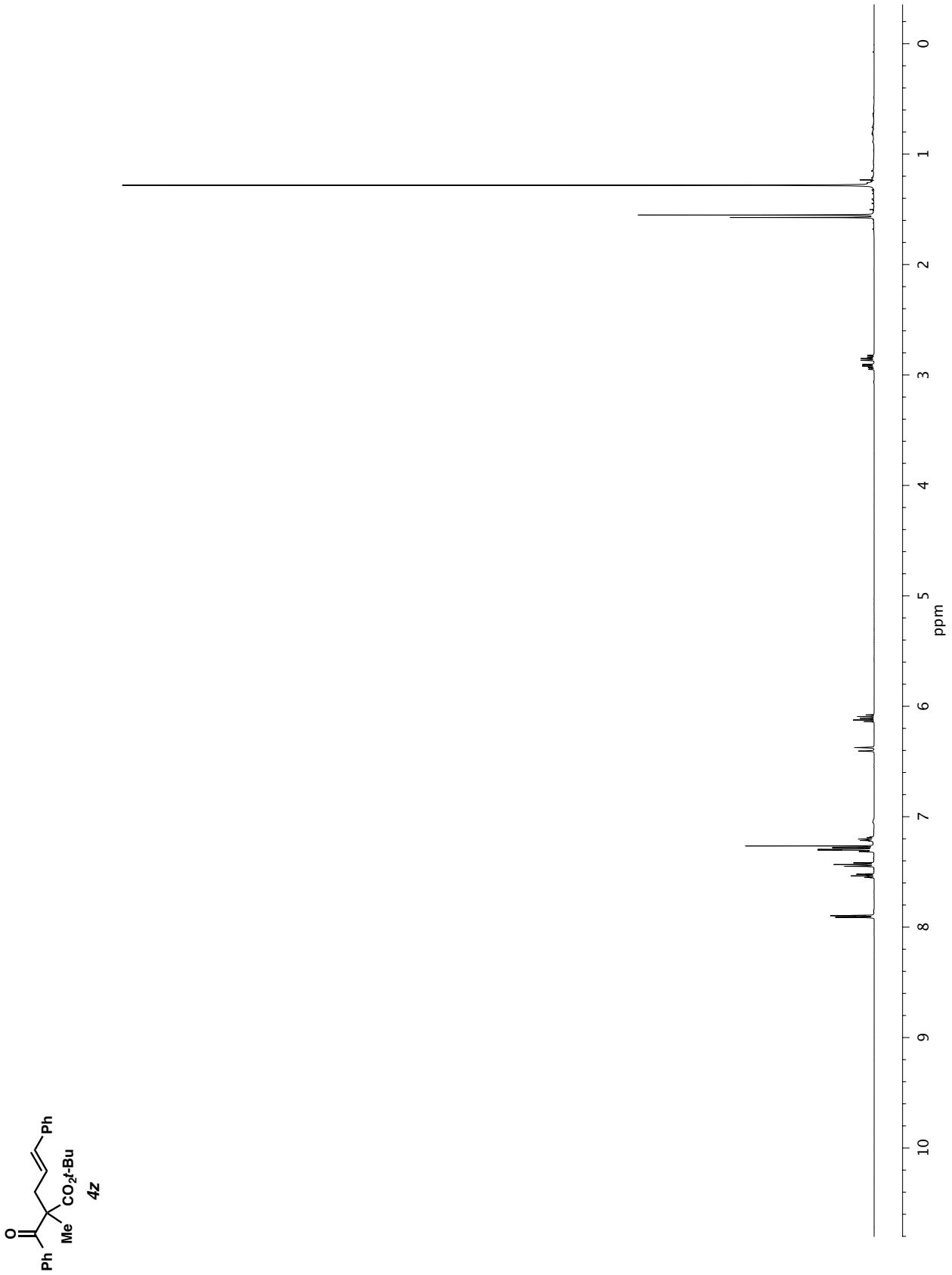
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3z**.



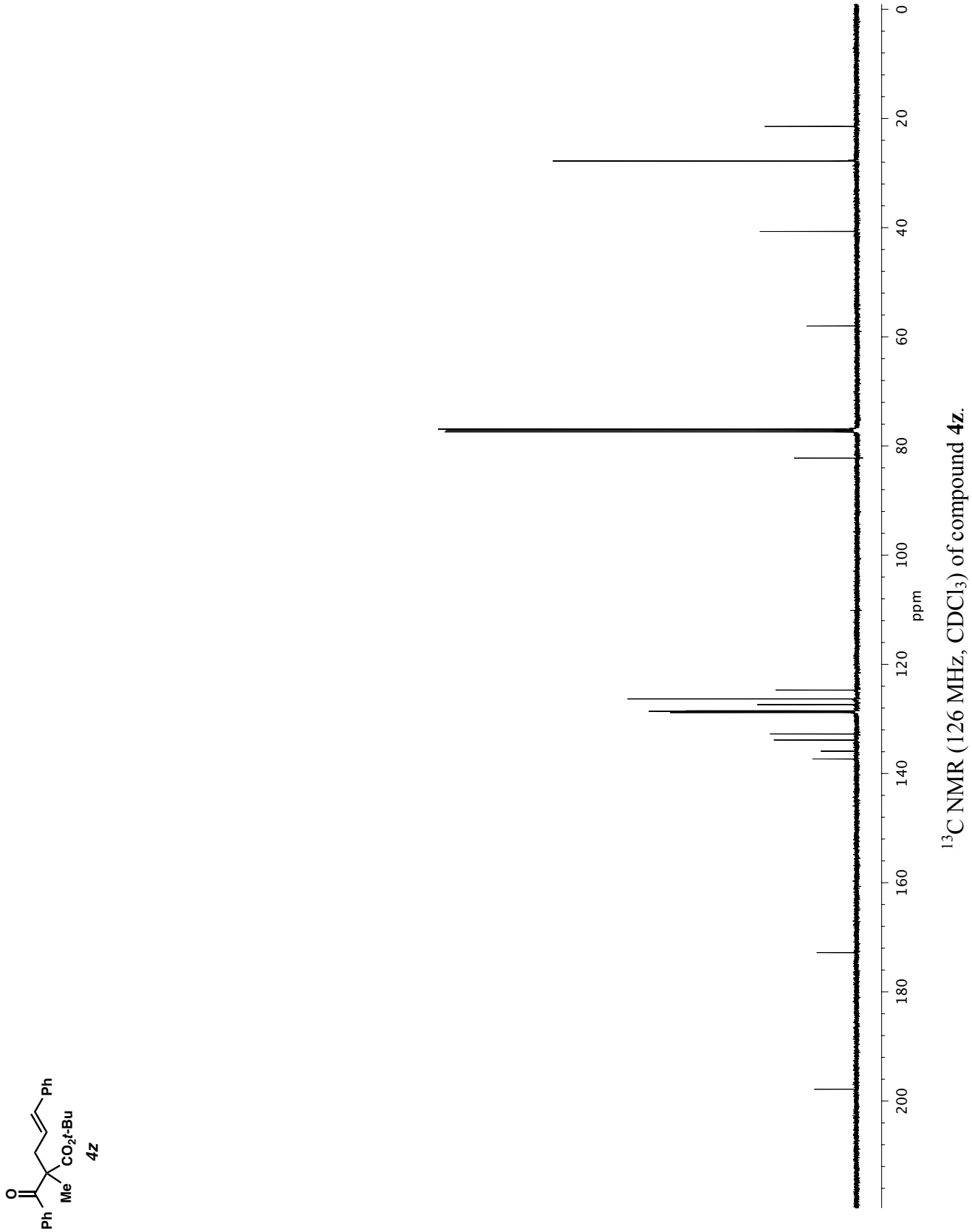
3z



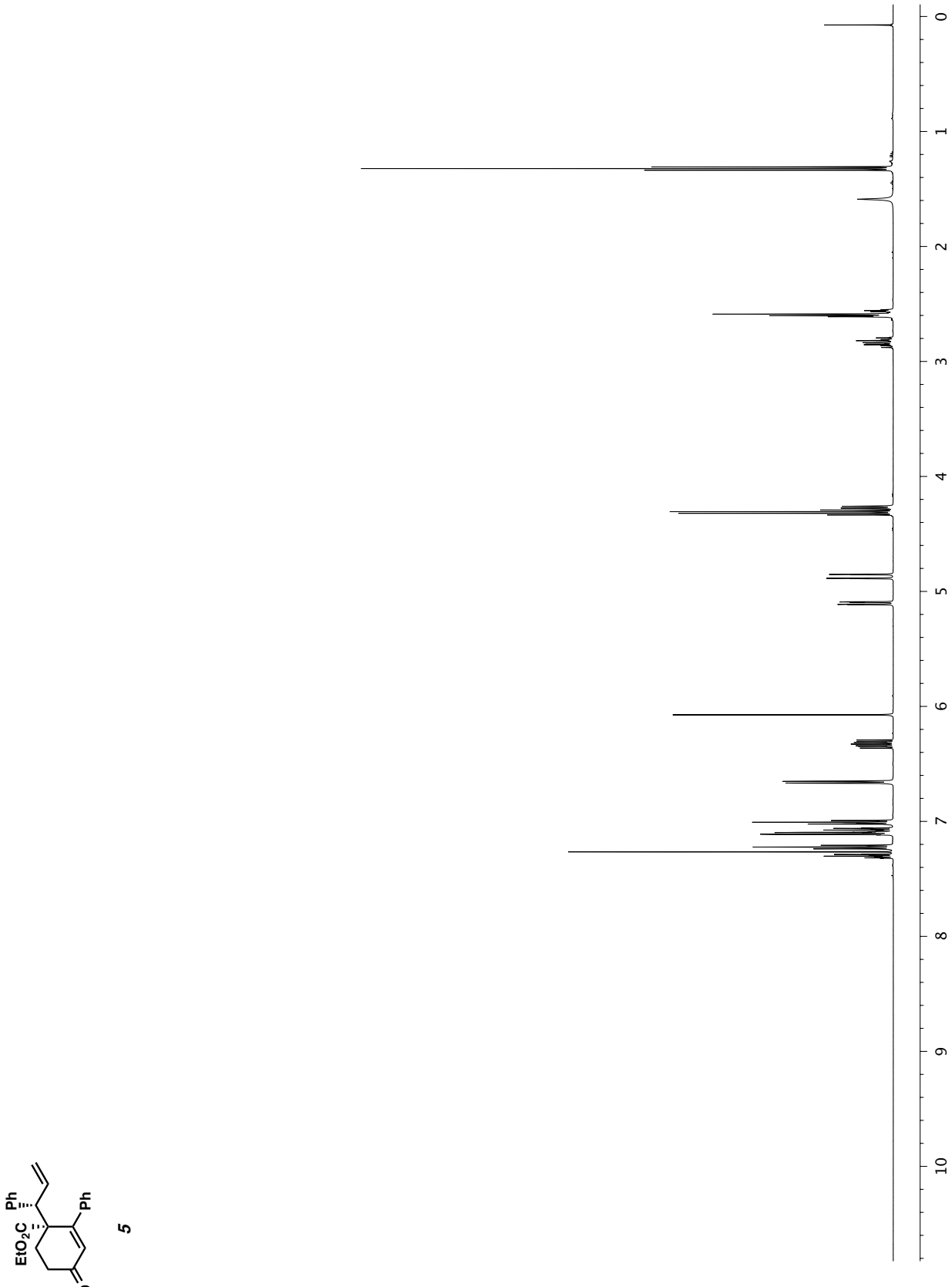
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3z**.



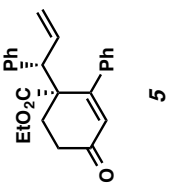
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4z**.



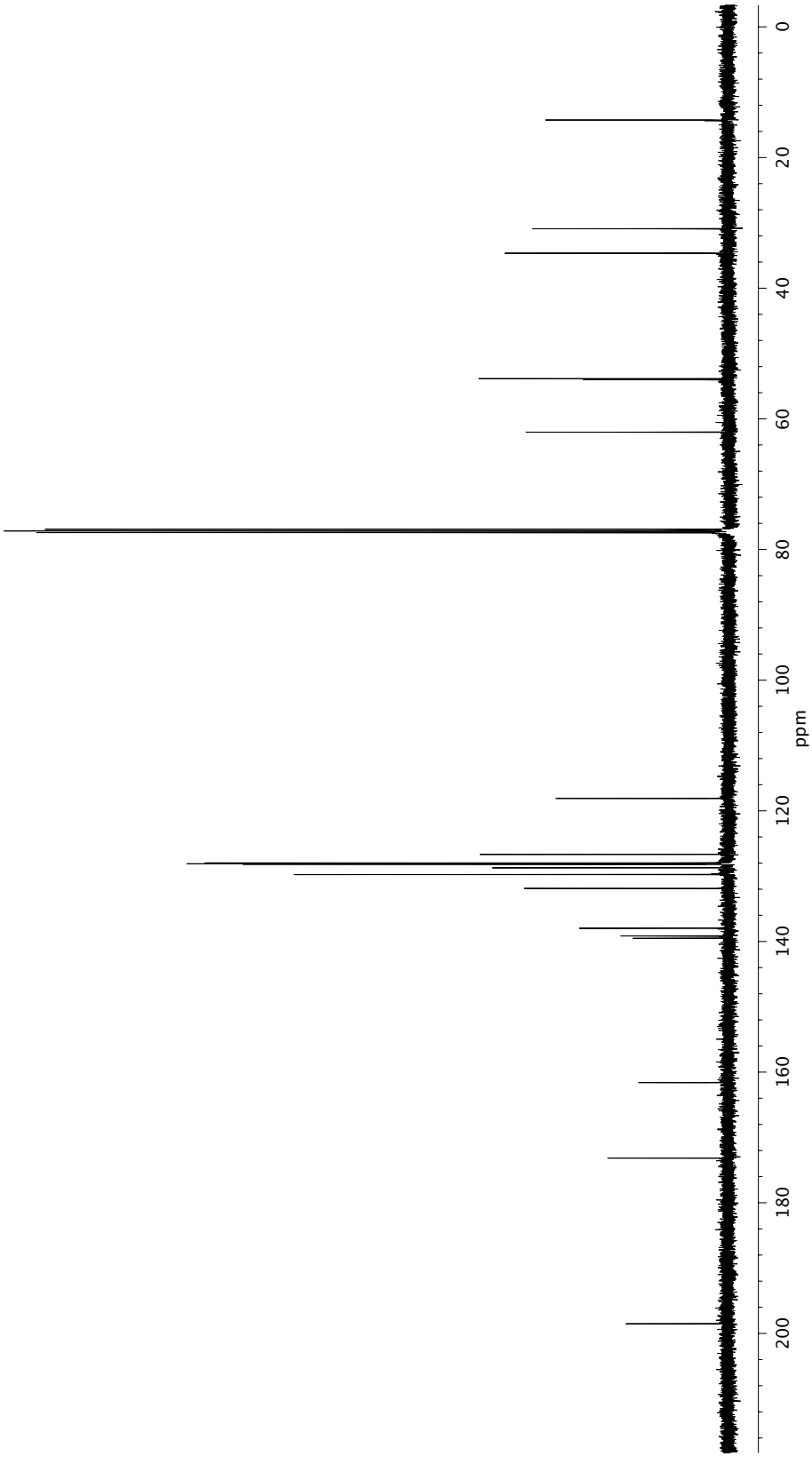
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4z**.



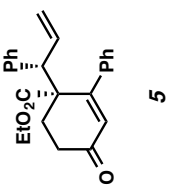
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**.



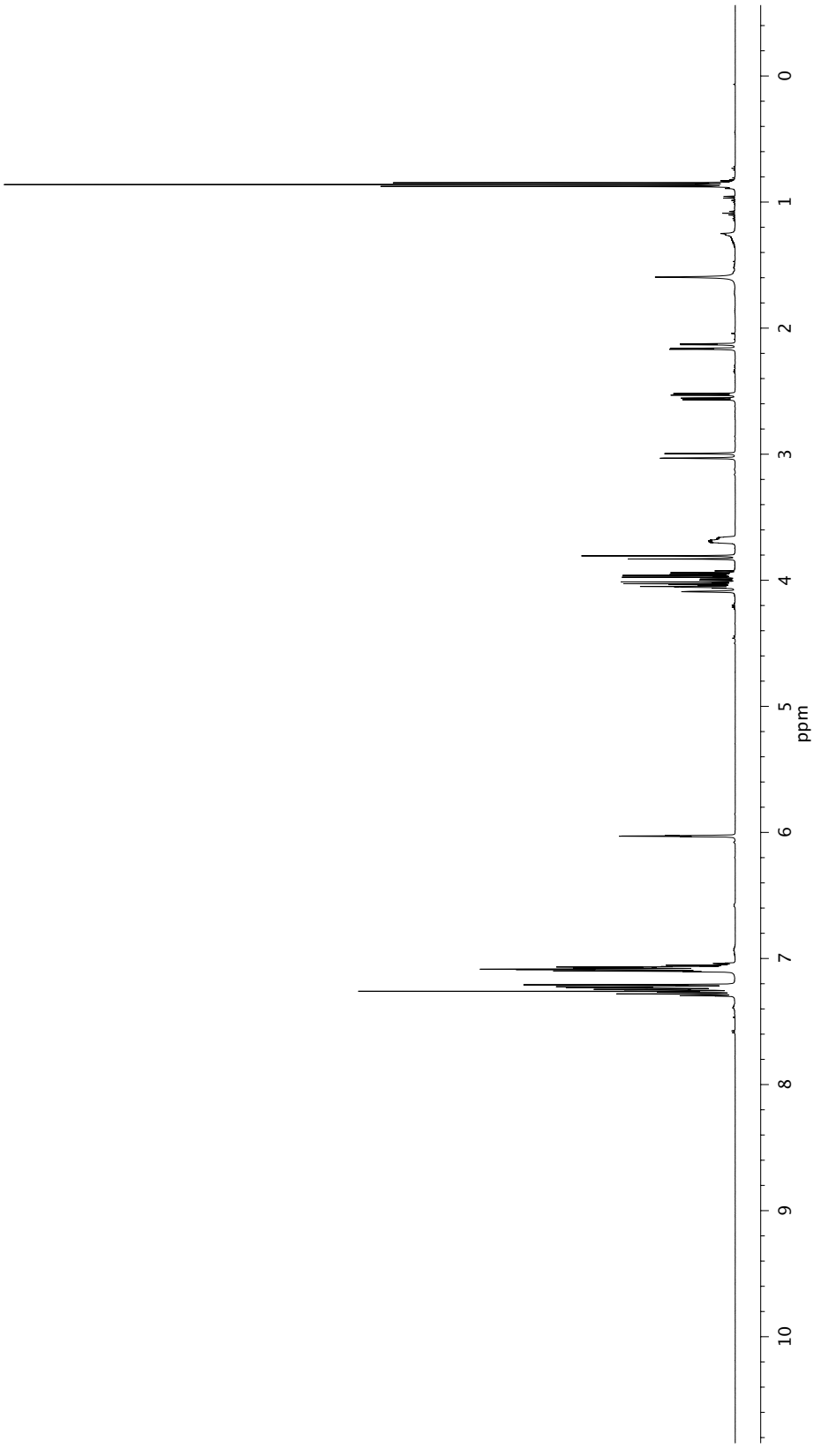
5



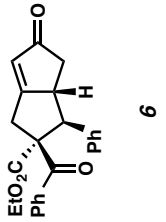
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5**.



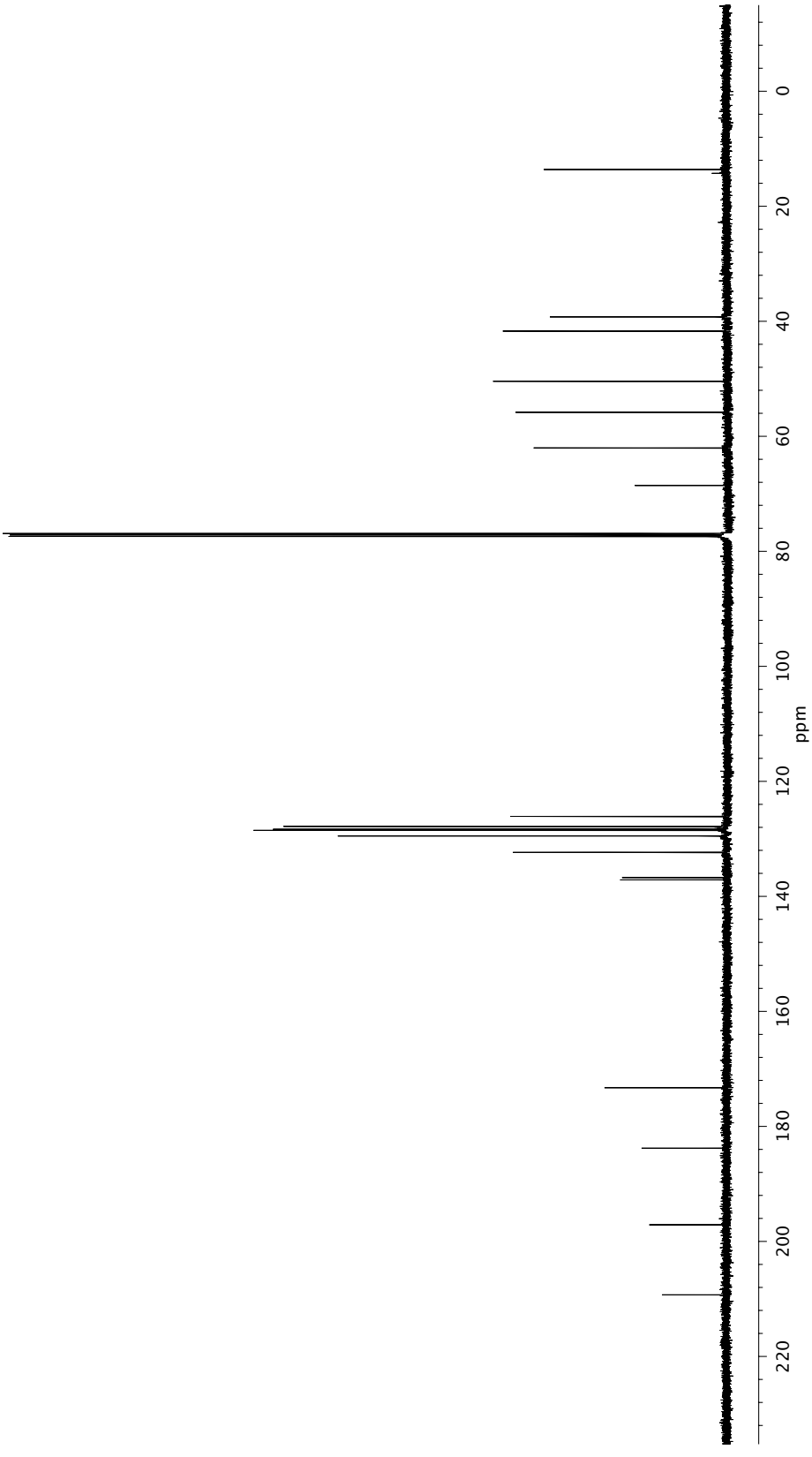
5



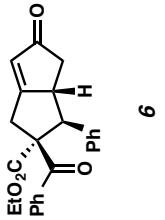
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



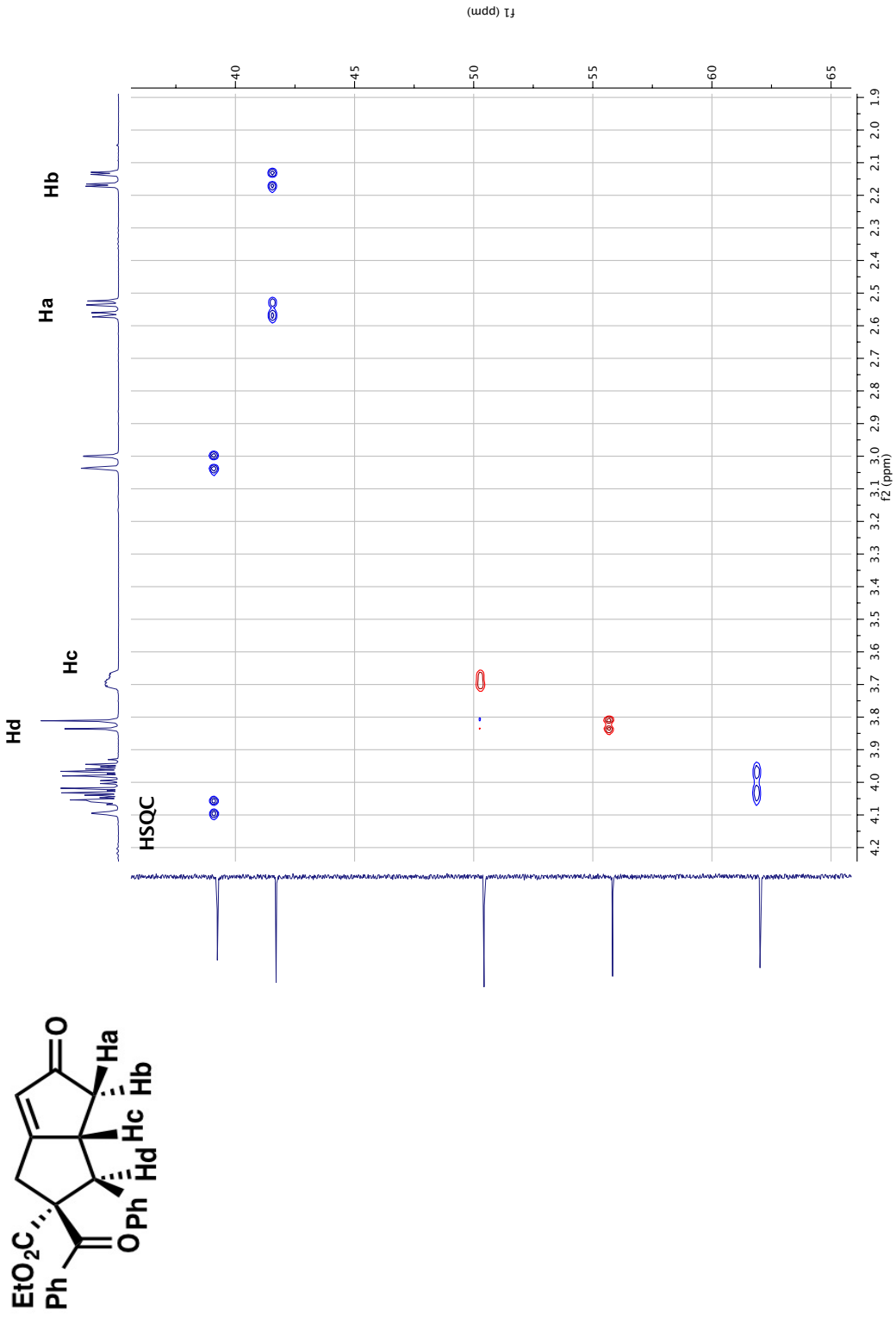
6



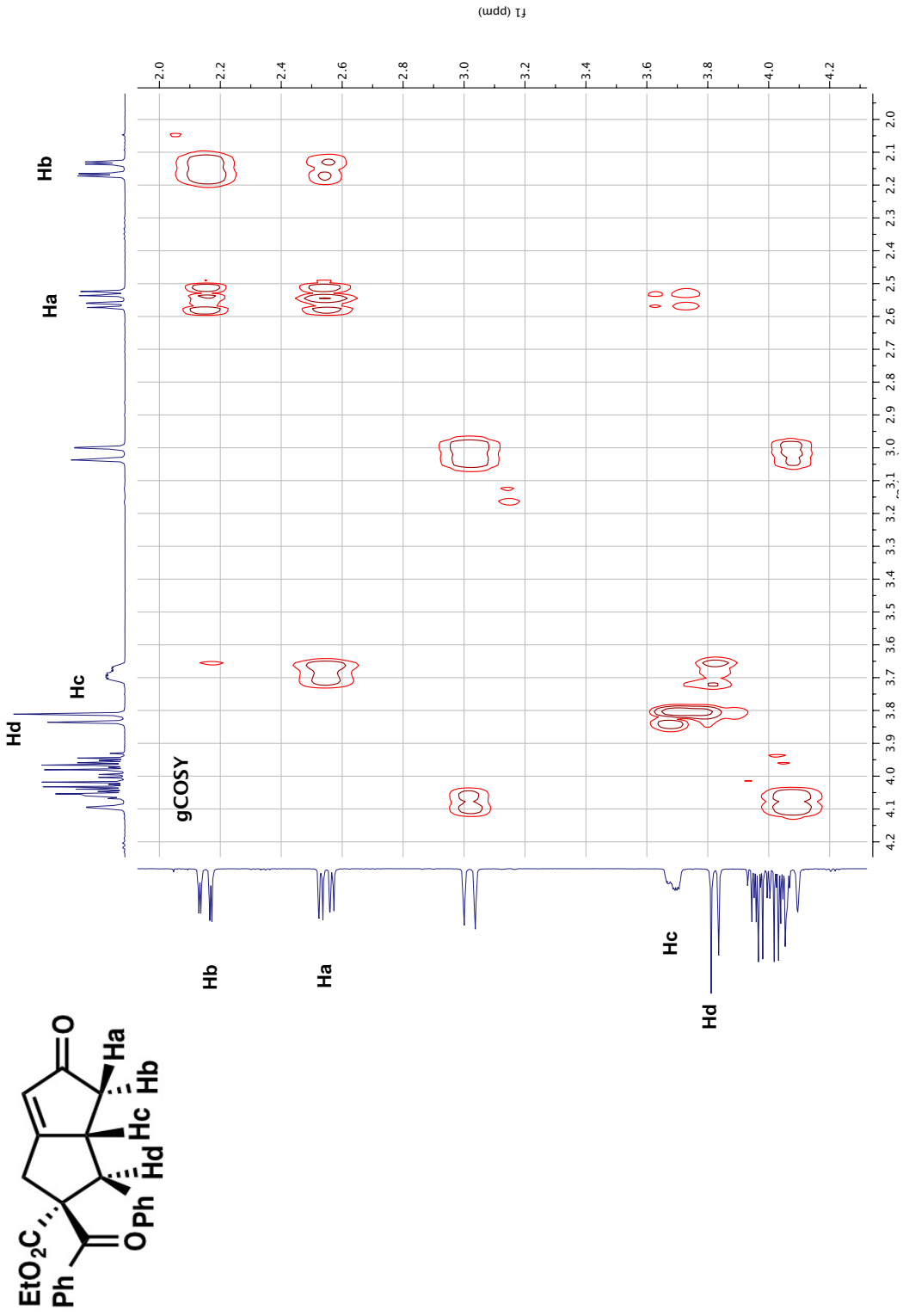
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6**.



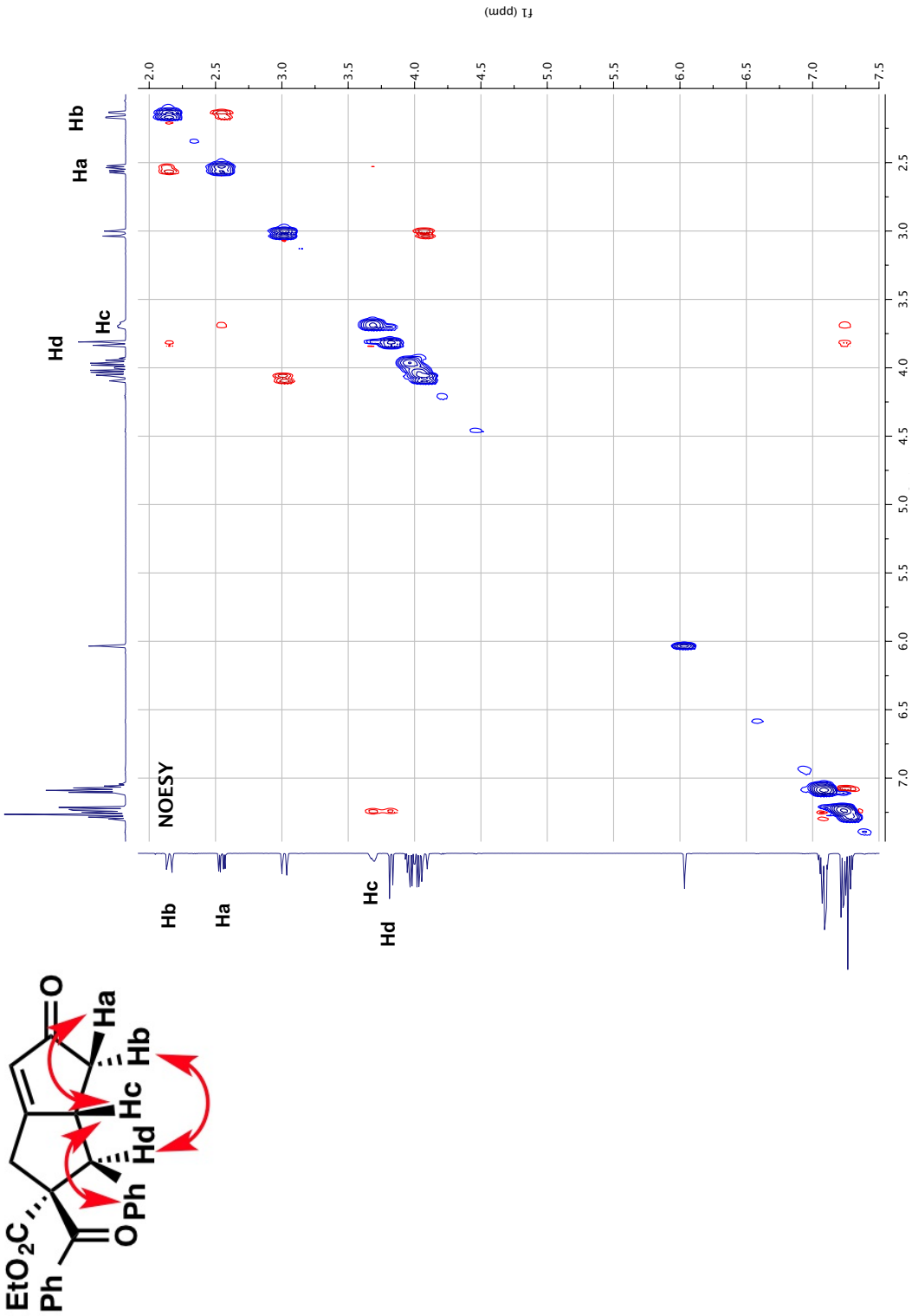
6



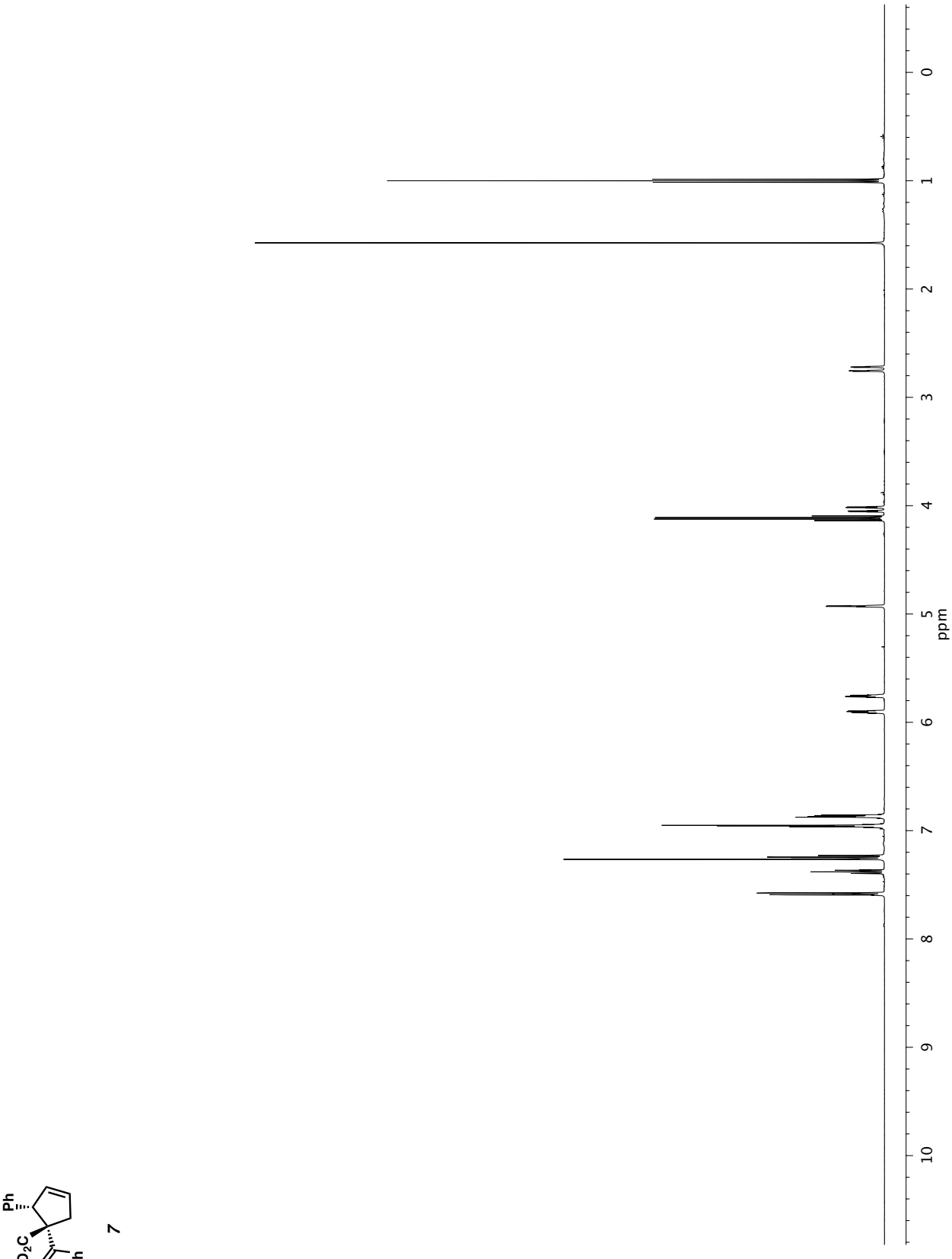
HSQC NMR (500 MHz, $CDCl_3$) of compound **6**.



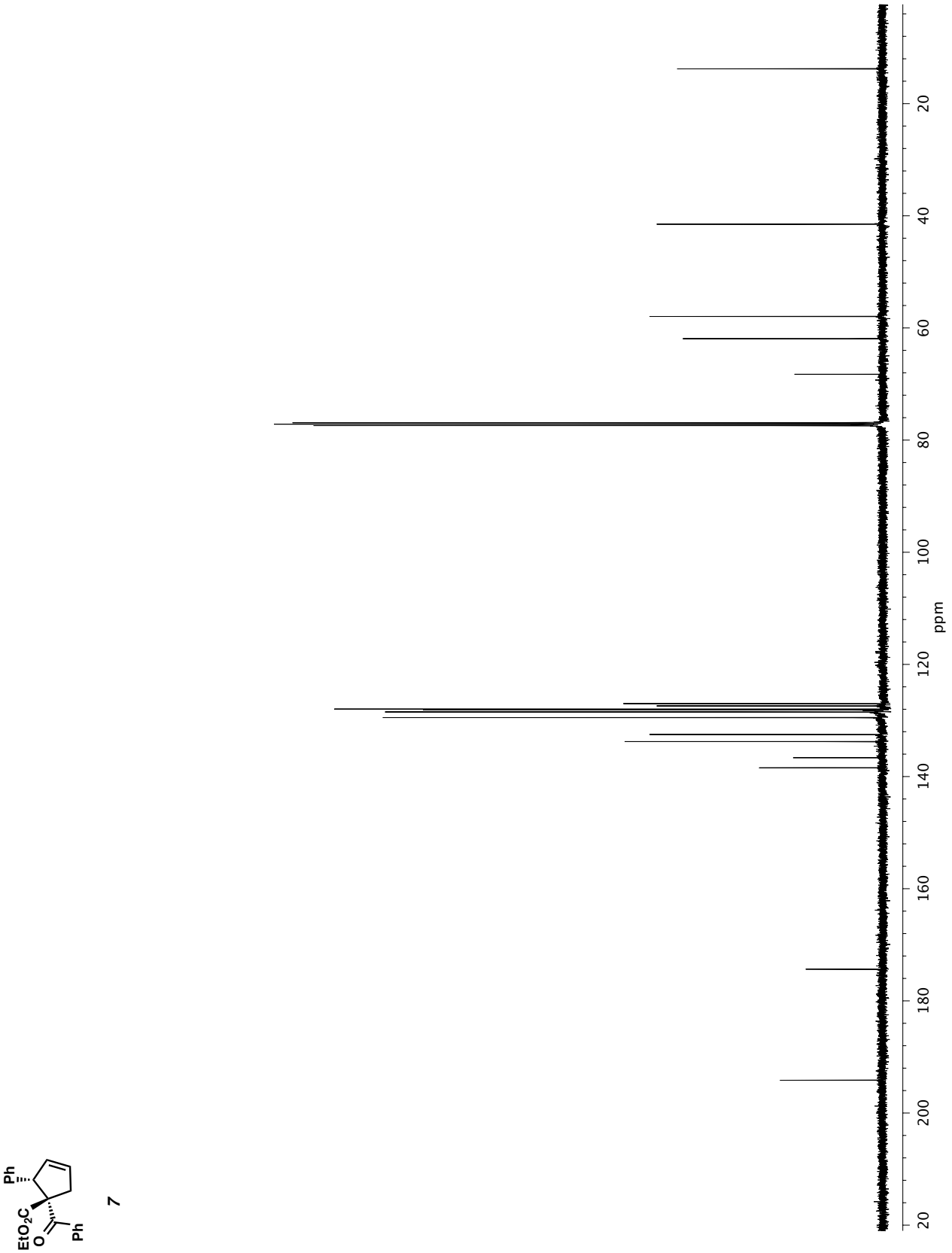
gCOSY NMR (500 MHz, $CDCl_3$) of compound **6**.



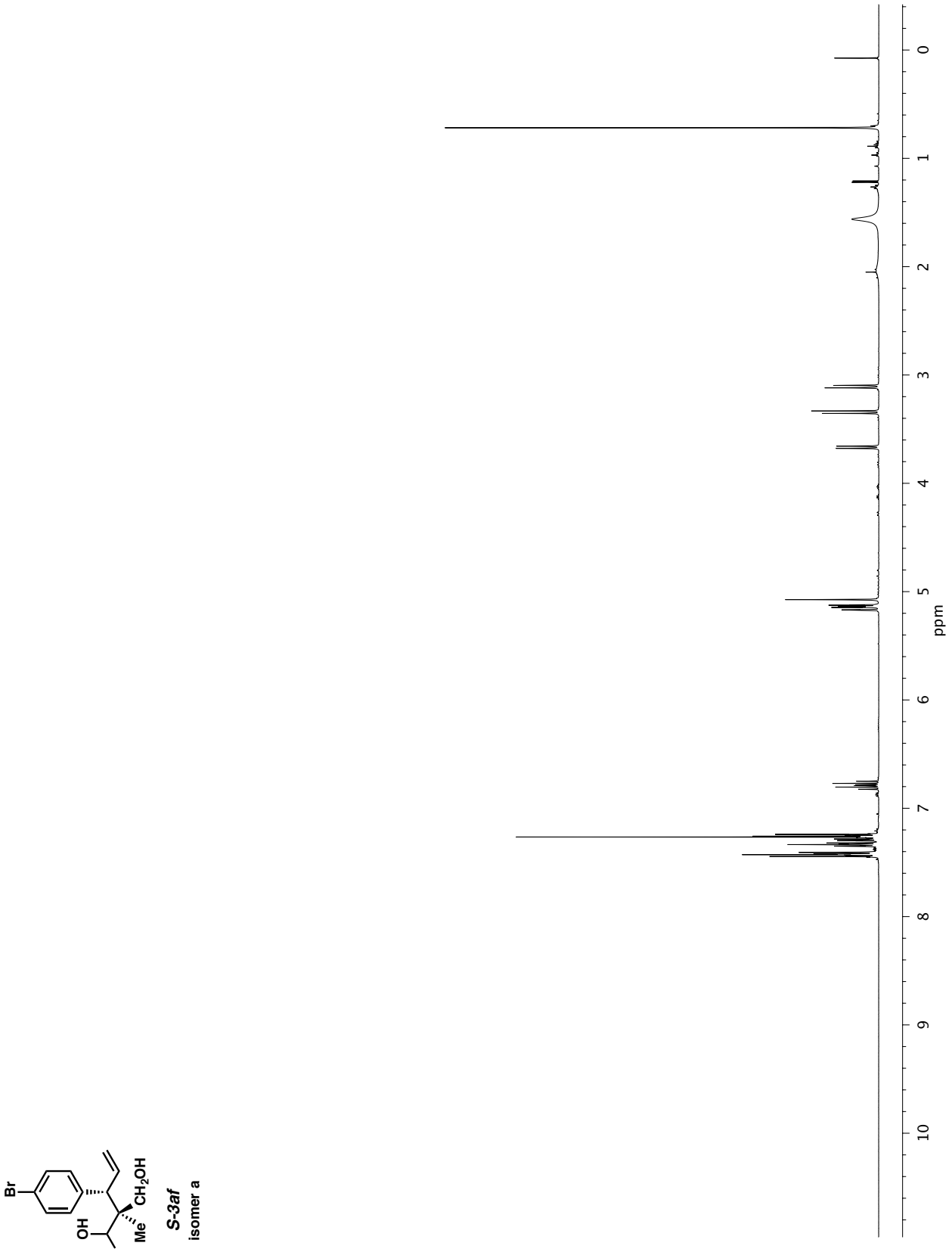
NOESY NMR (500 MHz, $CDCl_3$) of compound **6**.



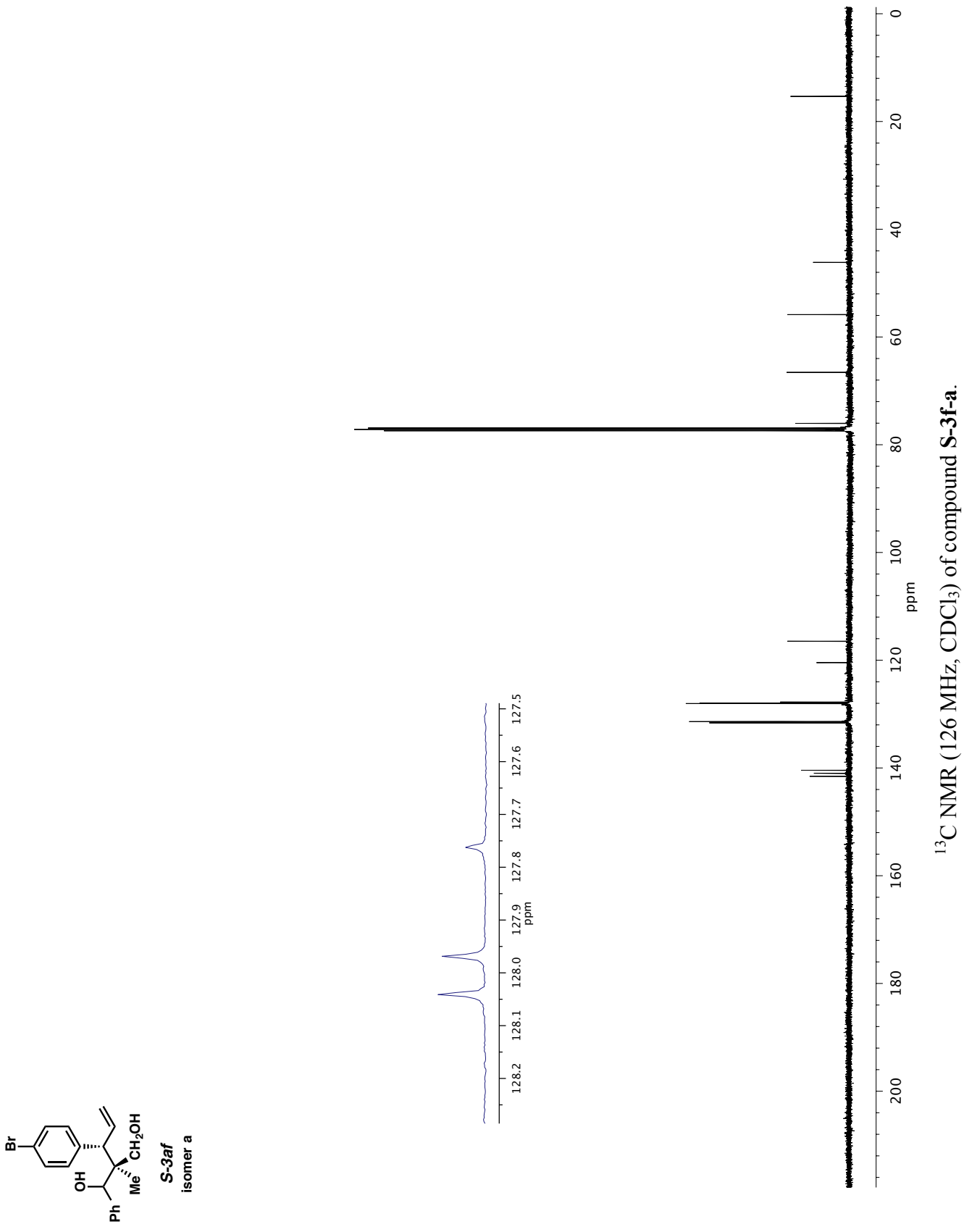
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.



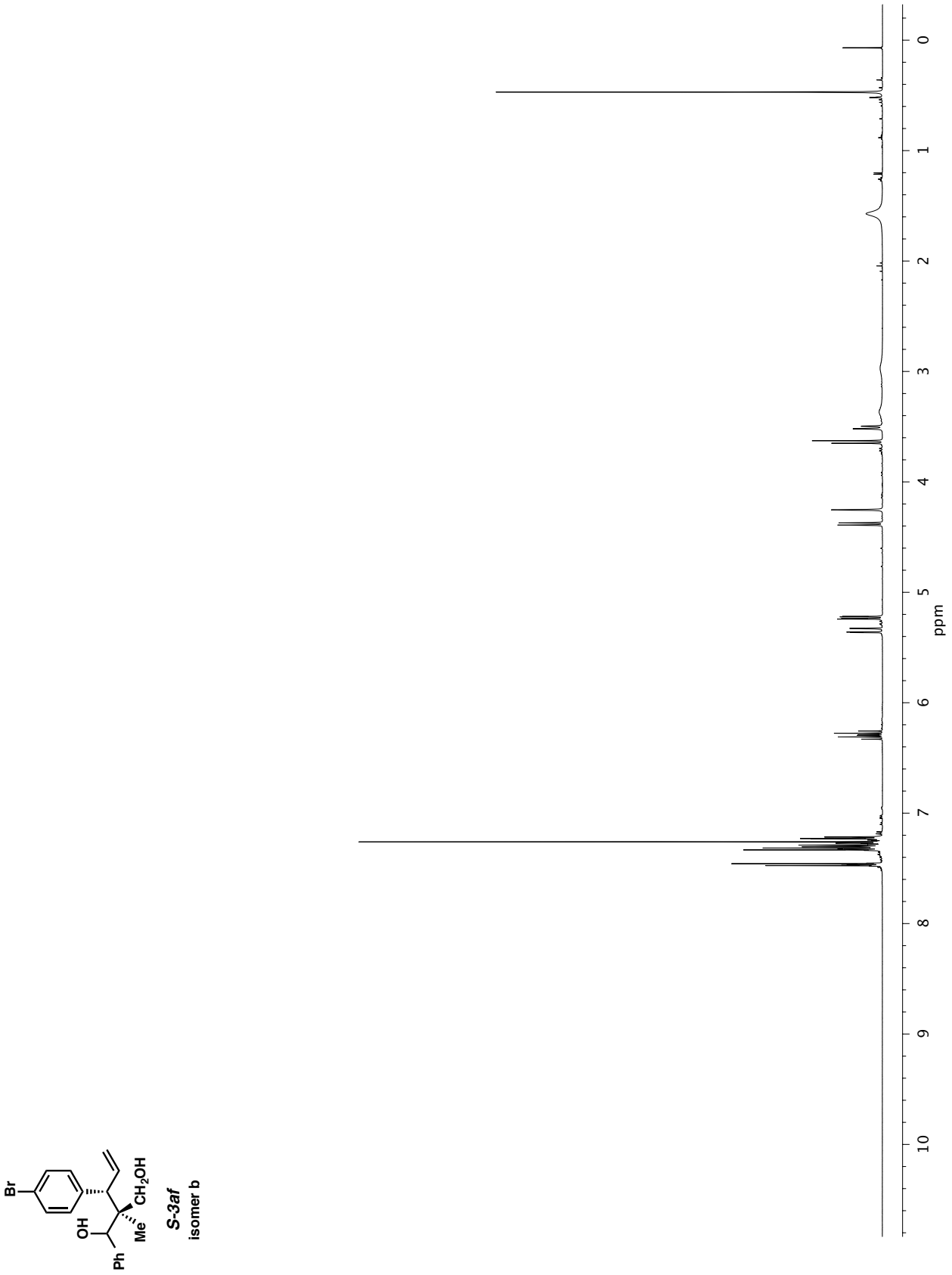
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7**.



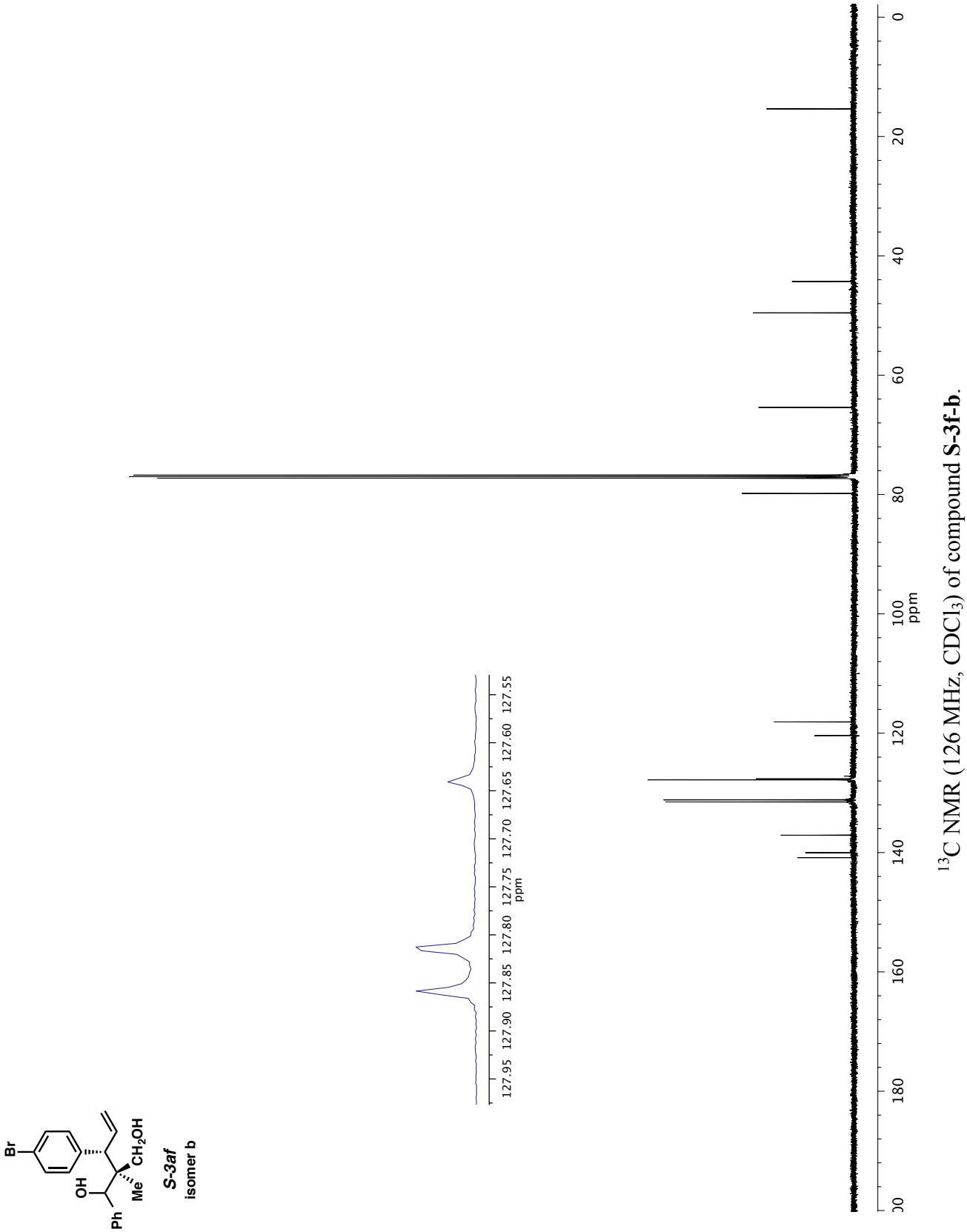
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S-3f-a**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **S-3f-a**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **S-3f-b**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **S-3f-b**.